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NEET JEE

Class XI







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THE p-BLOCK ELEMENTS (GROUP 13 and 14)

GROUP 13 ELEMENTS: BORON FAMILY

- $\lower \$ General electronic configuration : ns^2np^1
- Electronic configuration: B(5)-[He] $2s^22p^1$; Al(13)-[Ne] $3s^23p^1$; Ga(31)-[Ar] $3d^{10}4s^24p^1$; In(49)-[Kr] $4d^{10}5s^25p^1$; Tl(81)-[Xe] $4f^{14}5d^{10}6s^26p^1$; Uut(113)-[Rn] $5f^{14}6d^{10}7s^27p^1$

PHYSICAL PROPERTIES

Atomic radii

Increase from B to Al Decrease from Al to Ga Again increase from Ga to Tl.

Physical state

All are solids, B is non-metal. Al, Ga, In and Tl are silvery white metals.

Basic strength

 $B_2O_3 < Al_2O_3 < Ga_2O_3 < In_2O_3 < Tl_2O_3$ $B(OH)_3 < Al(OH)_3 < Ga(OH)_3 < In(OH)_3$ < Tl(OH)

Lewis acid character

 $BX_3 > AlX_3 > GaX_3 > InX_3$ (X = F, Cl, Br, I) $BF_3 < BCl_3 < BBr_3 < BI_3$

Stability of +1 oxidation state

Increases down the group $B^+ < Al^+ < Ga^+ < In^+ < Tl^+$

Stability of +3 oxidation state

Decreases down the group $B^{3+} > Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$

Ionic radii

Increase down the group $B^{3+} < Al^{3+} < Ga^{3+} < In^{3+} < Tl^{3+}$

Ionisation enthalpy

Shows irregular trend B > Tl > Ga > Al > In.

Electronegativity

Decreases from B to Al Increases from Al to Tl

Metallic or electropositive character

Increases from B to Al Decreases from Al to Tl

Density

Increases down the group B < Al < Ga < In < Tl

Melting points

Decreases sharply from B to Ga Increases from Ga to Tl

Boiling points

Decreases down the group B > Al > Ga > In > Tl

Physical **Properties**

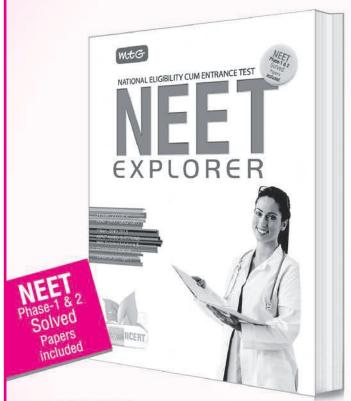
Atomic and

Reducing character Decreases down the group Al > Ga > In > Tl

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CHEMICAL PROPERTIES

Action with air

 $4M + 3O_2 \xrightarrow{\text{High temp.}} 2M_2O_3 \text{ (Tl forms Tl}_2O + \text{Tl}_2O_3)$

Action with alkalies

$$2B + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2$$

$$2M + 2NaOH + 2H_2O \longrightarrow 2NaMO_2 + 3H_2$$

$$(M = Al, Ga)$$
or $2M + 2NaOH + 6H_2O \longrightarrow$

$$2Na[M(OH)_4] + 3H_2$$

$$(M = Al, Ga)$$

Action with acids

B + 3HNO₃
$$\xrightarrow{\text{conc. H}_2\text{SO}_4}$$
 \rightarrow H₃BO₃ + 3NO₂
2B + 3H₂SO_{4(conc.)} $\xrightarrow{\Delta}$ 2H₃BO₃ + 3SO₂
2Al + 6HCl \longrightarrow 2AlCl₃ + 3H₂
2Tl + 3H₂SO₄ \longrightarrow Tl₂(SO₄)₃ + 3H₂
(Ga and Al become passive in conc. HNO₃ due to oxide layer formation.)

Action with nitrogen

$$2B + N_2 \xrightarrow{\text{High temp.}} 2BN, 2Al + N_2 \longrightarrow 2AlN$$

Action with halogens

 $2M + 3X_2 \xrightarrow{\text{High temp.}} 2MX_3 (X = F, Cl, Br, I)$

Action with carbon

 $4B + C \xrightarrow{\Delta} B_4C$
 $4Al + 3C \xrightarrow{\Delta} Al_4C_3$

Group 13 Elements

 $3Mg + 2B \xrightarrow{\Delta} Mg_3B_2$ Action with ammonia

Action with metals

 $2M + 2NH_3 \longrightarrow 2MN + 3H_2$

Action with water

$$2B + 3H_2O \longrightarrow B_2O_3 + 3H_2$$
(Red hot) (Steam)
$$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2$$
Cold water
$$4Tl + 2H_2O + O_2 \longrightarrow 4TlOH$$
(Ga and In react with water only in presence of O_2)

Anomalous Behaviour of Boron

- Boron shows anomalous behaviour due to its small size, high nuclear charge, high electronegativity and non-availability of *d*-electrons.
- The main points of differences are as follows:
 - > Boron is a typical non-metal whereas other members are metals.
 - It alone exhibits allotropy.
 - It is a bad conductor of electricity whereas others are good conductors.
- It forms only covalent compounds whereas other elements also form some ionic compounds.
- Hydroxides and oxides of boron are weakly acidic in nature whereas those of others are amphoteric and basic.
- The trihalides of boron (BX_3) exist as monomer whereas others exist as dimers.
- It exhibits maximum covalency of 4 while others exhibit a maximum covalency of 6.

IMPORTANT COMPOUNDS OF B AND AI

Structure

 $p\pi$ - $p\pi$ -back bonding

Preparation

$$B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O$$

Boron trifluoride

Uses

- It acts as a catalyst in organic reactions.
- It is used as an important reagent in organic chemistry as a Lewis acid.

Properties

• It undergoes rapid halide exchange reactions.

$$BF_3 + BCl_3 \longrightarrow BF_2Cl + BCl_2F$$

• It is electron deficient hence, acts as Lewis acid that forms adducts with Lewis bases.

$$BF_3 + (C_2H_5)_2O \longrightarrow BF_3.O(C_2H_5)_2$$

• It reacts with water to give boric acid and fluoroboric

$$4BF_3 + 3H_2O \longrightarrow 3HBF_4 + B(OH)_3$$

Structure
OH

$$B^{-}$$

O O B-OH
 OH
 OH
 OH
 OH

(Na₂B₄O₇·10H₂O) Borax

Uses

- As water softener and cleansing agent.
- In the laboratory for borax bead test.
- It is used in the manufacture of heat resistant borosilicate glass (pyrex). It is used as a stiffening agent for candle milks and used for glazing paper and playing cards.

Structure

Properties

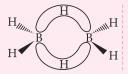
• It is a weak monobasic acid. It is not a protonic acid but acts as Lewis acid.

 $B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$

Action of heat:

- H₃BO₃ · $HBO_2 + H_2O$ Boric acid Metaboric acid
- \rightarrow H₂B₄O₇ $\xrightarrow{\text{Red}}$ 2B₂O₃ + H₂O • 4HBO₂ Tetraboric Metaboric trioxide acid

Structure



Four 2c-2e B-H terminal bonds Two 3*c*-2*e* B-H bridging bonds

• $4BF_3 \cdot Et_2O + 3LiAlH_4 \xrightarrow{Diethyl} 2B_2H_6 + 3LiF + 3AlF_3 + 4Et_2O$

Laboratory Method :

- $2\text{NaBH}_4 + \text{I}_2 \longrightarrow \text{B}_2\text{H}_6 + 2\text{NaI} + \text{H}_2$ Industrial Method :
- $2BF_3 + 6NaH \xrightarrow{450 \text{ K}} B_2H_6 + 6NaF$

Preparation

• From colemanite:

$$Ca_2B_6O_{11} + 2Na_2CO_3 \xrightarrow{\Delta} 2CaCO_3 \downarrow + Na_2B_4O_7 + 2NaBO_2$$

 $4NaBO_2 + CO_2 \xrightarrow{} Na_2CO_3 + Na_2B_4O_7$
 $4H_3BO_3 + Na_2CO_3 \xrightarrow{} Na_2B_4O_7 + 6H_2O + CO_2$
On cooling, crystals of borax, *i.e.*, $Na_2B_4O_7 \cdot 10H_2O$ separate out.

Properties

- Its aqueous solution is basic in nature due to hydrolysis. $Na_2B_4O_7 + 2H_2O \Longrightarrow 2NaOH + H_2B_4O_7$ Strong base Weak acid
- Action of heat:

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{740^{\circ}C} 2NaBO_2 + B_2O_3$$
Anhydrous

Transparent bead

• Action of ethyl alcohol and sulphuric acid:

$$\begin{aligned} &\text{Na}_2 \text{B}_4 \text{O}_7 + \text{H}_2 \text{SO}_4 + 5 \text{H}_2 \text{O} \Longrightarrow \text{Na}_2 \text{SO}_4 + 4 \text{H}_3 \text{BO}_3 \\ &\text{H}_3 \text{BO}_3 + 3 \text{C}_2 \text{H}_5 \text{OH} \Longrightarrow \text{B}(\text{OC}_2 \text{H}_5)_3 + 3 \text{H}_2 \text{O} \end{aligned}$$

Triethyl borate

Preparation

• From borax:

 $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 4H_3BO_3 + 2NaCl$ $Na_2B_4O_7 + H_2SO_4 + 5H_2O \longrightarrow 4H_3BO_3 + Na_2SO_4$

• By hydrolysis of boron compounds: $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

 $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$

 $BN + 3H_2O \longrightarrow H_3BO_3 + NH_3$

Uses

- It is used in the manufacture of heat resistant borosilicate glass.
- The aqueous solution of boric acid is used as a mild antiseptic especially as eye wash under the name boric lotion.
- It is used as a food preservative in food industry.
- It is used in the manufacture of pigments and borax.

Properties

- $B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$
- $2NaH + B_2H_6 \xrightarrow{\text{Diethyl}} 2Na^+[BH_4]^-$ Sod. hydride Sod. borohydride
- 2LiH + B_2H_6 Diethyl $2Li^{\dagger}[BH_4]^{-}$ Lithium hydride Lithium borohydride
- \Rightarrow 3[BH₂(NH₃)₂]⁺[BH₄]⁻ $\xrightarrow{\Delta}$ • $3B_2H_6 + 6NH_3$ $2B_3N_3H_6 + 12H_2$ Inorganic benzene

Uses

- For preparing a number of borohydrides such as LiBH₄, NaBH₄, etc.
- As a reducing agent in organic reactions.

Preparation

- $2Al + 3Cl_2 \longrightarrow 2AlCl_3$
- $2Al + 6HCl \longrightarrow 2AlCl_3 + 3H_2$

• Al₂O₃ + 3C + 3Cl₂
$$\xrightarrow{100^{\circ}\text{C}}$$
 2AlCl₃ + 3CO

Properties

- Anhydrous AlCl₃ fumes in moist air due to hydrolysis and the resulting solution is acidic.
- AlCl₃ + $3H_2O \longrightarrow Al(OH)_3 + 3HCl$
- AlCl₃ + 3NH₄OH \longrightarrow Al(OH)₃ \downarrow + 3NH₄Cl

Gelatinous ppt. (Insoluble in NH₄OH)

• AlCl₃ + 3NaOH \longrightarrow Al(OH)₃ \downarrow + 3NaCl

(Soluble in excess NaOH)

• Al(OH)₃ + NaOH \longrightarrow NaAlO₂ + 2H₂O (Soluble meta aluminate)

Uses

• Anhydrous AlCl₃ is used as a catalyst in Friedel—Crafts reaction and in cracking of petroleum.

Aluminium chloride

AICI3

ALUMS

These are double sulphates with general formula,

 $M_2SO_4 \cdot M_2'(SO_4)_3.24H_2O$

where M stands for a monovalent metal or radical, e.g., Na^+ , K^+ , NH_4^+ , etc., while M' stands for a trivalent metal, e.g., Al^{3+} , Cr^{3+} , Fe^{3+} , etc.

Ammonia alum, (NH₄)₂SO₄.Al₂(SO₄)₃.24H₂O

Chrome alum, K₂SO₄.Cr₂(SO₄)₃.24H₂O

Ferric ammonia alum, (NH₄)₂SO₄.Fe₂(SO₄)₃.24H₂O

Sodium alum, Na₂SO₄.Al₂(SO₄)₃.24H₂O

Potash alum, K₂SO₄.Al₂(SO₄)₃.24H₂O



Aluminium: Its likely contribution to Alzheimer's disease!

he biological availability of aluminium or the ease with which aluminium reacts with human biochemistry means that aluminium in the body is unlikely to be benign, though it may appear as such due to the inherent robustness of human physiology. The accumulation of aluminium in the brain will achieve a toxic threshold and a specific neurone or area of the brain will stop coping with the presence of aluminium and will start reacting to its presence. If the same neurone or brain tissue is also suffering other insults, or another on-going degenerative condition then the additional response to aluminium will exacerbate these effects. In this way aluminium may cause a particular condition to be more aggressive and perhaps to have an earlier onset such occurrences have already been shown in Alzheimer's disease related to environmental and occupational exposure to aluminium."

"There are neither cures nor effective treatments for Alzheimer's disease. The role of aluminium in Alzheimer's disease can be prevented by reducing human exposure to aluminium and by removing aluminium from the body by non-invasive means.

GROUP 14 ELEMENTS: CARBON FAMILY

PHYSICAL PROPERTIES

- General electronic configuration : ns^2np^2
- Electronic configuration : C(6)-[He] $2s^22p^2$, Si(14)-[Ne] $3s^23p^2$, Ge(32)-[Ar] $3d^{10}4s^24p^2$, Sn(50)-[Kr] $4d^{10}5s^25p^2$, **Pb(82)**-[Xe] $4f^{14}5d^{10}6s^{2}6p^{2}$, **Uuq(114)**-[Rn] $5f^{14}6d^{10}7s^{2}7p^{2}$

Atomic and

Physical Properties

Atomic radii

Increase down the group.

C < Si < Ge < Sn < Pb

Density

Increases down the group from C to Pb.

Melting and Boiling points

Decrease down the group. However, m.pt. of tin is lower than that of lead.

Catenation

Decreases down the group.

 $C \gg Si \gg Ge \approx Sn \gg Pb$

Ionisation enthalpy

Decreases down the group with increase in the atomic radii and small increase from Sn to Pb. C > Si > Ge > Sn < Pb

Electronegativity

Decreases as we move down the group but not after silicon.

 $C > Si \simeq Ge \simeq Sn < Pb$

Oxidation states

Stability of +4 oxidation state decreases down the group. Stability of +2 oxidation state increases from Ge to Pb due to inert pair effect.

Metallic character

Increases down the group.

CHEMICAL PROPERTIES

Reactivity towards air

- They form oxides of the formula EO and EO₂ on heating with air.
- Acidic strength of their oxides decreases down the group. CO₂, SiO₂

Acidic

 GeO_2 Less acidic

SnO₂, PbO₂ Amphoteric

Reactivity towards halogens

- They form halides of the formula, EX_4 and EX_2 .
- Except C, all react directly with halogens.
- Except C and Si, all form dihalides.

Reactivity towards water

- C, Si and Ge do not decompose water.
- Only Sn can decompose steam.
- $Sn + 2H_2O \xrightarrow{\Delta} SnO_2 + 2H_2$
- Pb is unaffected by water due to the formation of a protective oxide

Chemical **Properties**

Reactivity with alkalies

- Carbon is unaffected by alkalies.
- Si reacts slowly with cold aqueous solution of NaOH and readily with hot solution forming

$$Si + 2KOH + H_2O \longrightarrow K_2SiO_3 + 2H_2$$

 Sn and Pb are slowly attacked by cold alkali and rapidly by hot alkali forming stannates and

$$Sn + 2NaOH + 4H_2O \longrightarrow Na_2[Sn(OH)_6] + 2H_2$$

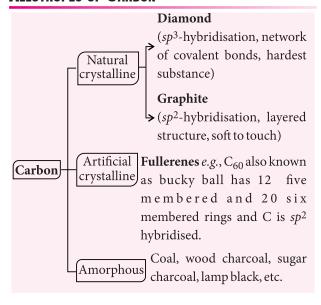
$$Pb + 2NaOH + 4H_2O \longrightarrow Na_2[Pb(OH)_6] + 2H_2$$

Sodium plumbate

Reactivity with acids

- Diamond is unaffected by concentrated acids, but graphite changes to mellitic acid C₆(COOH)₆ with alkaline KMnO₄ and oxidised to graphitic acid (C₁₁H₄O₅) with conc. HNO₃.
- C, Si, Ge are unaffected by dilute acids.
- Sn dissolves in dil. HNO₃. $4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3$ +3H₂O
- Pb dissolves slowly in dil. HCl and also dissolves in organic acids.
- Lead does not dissolve in dil. H₂SO₄ and conc. HCl because a surface coating of PbSO₄ and PbCl₂ is formed.

ALLOTROPES OF CARBON



Carbon dioxide

Anomalous Behaviour of Carbon

- Carbon differs from rest of the members of group 14 because of its small size, high electronegativity, property of catenation and absence of *d*-orbitals.
- The main points of differences are as follows:
 - The melting and boiling points, ionisation energy and electronegativity of carbon are very high as compared to the rest of the members of the group.
 - It has maximum tendency to show catenation as compared to other members of the group.
 - It has a high tendency to form $p\pi$ - $p\pi$ multiple bonds while others form $p\pi$ - $d\pi$ bonds and that is also to a lesser extent.
 - \triangleright CO₂ is a gas while the dioxides of all other members are solids.

IMPORTANT COMPOUNDS OF C AND SI

Preparation

•
$$C_{(s)} + O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$$

• $CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)}$

•
$$CH_{4(g)} + 2O_{2(g)} \xrightarrow{\Delta} CO_{2(g)} + 2H_2O_{(g)}$$

•
$$CaCO_{3(s)} + 2HCl_{(aq)}$$

 $\rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$

Properties

• It is an acidic oxide, and reacts with bases forming salts. $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

$$CO_2 + K_2CO_3 + H_2O \longrightarrow KHCO_3$$

- Solid CO₂ is called 'dry ice' and is used to freeze foods and ice-cream.

• It is consumed during photosynthesis.

$$6CO_2 + 12H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

- In aerated water, e.g., in soda water, etc.
- In extinguishing fire.
- Solid carbon dioxide (dry ice) is used as refrigerant.
- As carbogen [mixture of $O_2 + CO_2$ (5-10%)] in artificial respiration especially for pneumonia patients and victims of CO poisoning.

Structure

Preparation

•
$$2C_{(s)} + O_{2(g)} \xrightarrow{\Delta} 2CO_{(g)}$$

• HCOOH
$$\frac{373 \text{ K}}{\text{Conc. H}_2\text{SO}_4}$$
 $\text{H}_2\text{O} + \text{CO}$

•
$$C_{(s)} + H_2O_{(g)} \xrightarrow{473 - 1273 \text{ K}} \underbrace{CO + H_2}_{\text{Water gas}}$$

•
$$2C + O_2 + 4N_2 \xrightarrow{473 - 1273 \text{ K}} \xrightarrow{2CO + 4N_2} \xrightarrow{\text{Producer gas}}$$

Properties

- Highly poisonous due to the ability to form a complex with haemoglobin (Hb) which is 300 times more stable than O₂-Hb complex thus, prevents Hb in the RBCs from carrying O_2 around the body.
- It is a powerful reducing agent and reduces many metal oxides to the metal.
- CO molecule acts as a donor and reacts with metals to form metal carbonyls.

Uses

- As an important constituent of two industrial fuels, i.e., water gas and producer gas.
- In Mond's process for purification of nickel via its nickel carbonyl.

Structure

Silicon dioxide

Properties

• Covalent, three dimensional network solid. Almost non-reactive due to high Si—O bond enthalpy. However, it is attacked by HF and NaOH.

$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

Uses

- Quartz is extensively used as a piezoelectric material.
- It has made possible to develop extremely accurate clocks, modern radio and television broadcasting and mobile radio communications.
- Silica gel is used as a drying agent and as a support for chromatographic materials and catalysts.
- Kieselguhr, an amorphous form of silica is used in filtration plants.

Structure



where R = alkyl or phenyl group

• Synthetic organosilicon polymers containing repeated *R*₂SiO units held by Si–O–Si linkage.

Properties

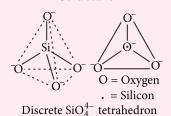
• They are water repelling due to non-polar alkyl groups.

Uses

• They are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

Silicates

Structure



where R = alkyl or phenyl group

Properties

- Basic unit is SiO₄⁴⁻.
- They exist either as discrete units or joined together by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit to form different structures like chain, ring, sheet or 3-D network.
- Zeolites are 3-D network silicates in which some of the Si atoms are replaced by Al³⁺ ions and to balance the negative charge some cations like Na⁺, K⁺ or Ca²⁺ are incorporated.

Uses

• They are used in water softening.

DIFFERENT TYPES OF SILICATES

- Orthosilicates contain discrete SiO₄⁴⁻ tetrahedra.
- $\$ Pyrosilicates contain $Si_2O_7^{6-}$ anion.
- $\" \$ Cyclic or ring silicates contain $(SiO_3)_n^{2n}$ anion.
- $\$ Chain silicates contain $(SiO_3^{2-})_n$ anions.
- $\$ Sheet silicates contain $(Si_2O_5^{2-})_n$ anions.
- Three dimensional silicates have three dimensional network structure.



1. In the following reaction sequence,

Metal $(A) + N_2 \xrightarrow{\Delta} (B) \xrightarrow{+H_2O} (C) + (D)$ white ppt. (C) formed is soluble in NaOH solution and gas (D) evolved gives white fumes in HCl. Metal A is

- (a) B
- (b) Al
- (c) Ga
- (d) C
- 2. The increasing order of atomic radii of the following group 13 elements is
 - (a) Al < Ga < In < Tl
- (b) Ga < Al < In < Tl
- (c) Al < In < Ga < Tl
- (d) Al < Ga < Tl < In

(JEE Advanced 2016)

- 3. Borax is used as a buffer since
 - (a) its aqueous solution contains equal amount of weak acid and its salt
 - (b) it is easily available
 - (c) its aqueous solution contains equal amount of strong acid and its salt
 - (d) none of these.
- 4. Which of the following statements is not correct?
 - (a) Silicon is extensively used as a semiconductor.
 - (b) Carborundum is SiC.
 - (c) Silicon occurs in free state in nature.
 - (d) Mica contains the element silicon.
- **5.** Match the items in column I with its main uses listed in column II.

Column I

Column II

- (A) Silica gel
- (i) Transistor
- (B) Silicon
- (ii) Ion-exchanger
- (C) Silicone
- (iii) Drying agent
- (D) Silicate
- (iv) Sealant
- (a) (A) (iii), (B) (i), (C) (iv), (D) (ii)
- (b) (A) (iv), (B) (i), (C) (ii), (D) (iii)
- (c) (A) (ii), (B) (i), (C) (iv), (D) (iii)
- (d) (A) (ii), (B) (iv), (C) (i), (D) (iii)

(JEE Main 2016 online)

- **6.** Lead pipes are not suitable for drinking water because
 - (a) a layer of lead dioxide is deposited over pipes
 - (b) lead forms basic lead carbonate

- (c) lead reacts with water and form poisonous lead salts
- (d) lead reacts with air to form litharge.
- 7. The bond present in borazole $(B_3N_3H_6)$ are
 - (a) 9σ , 6π
- (b) $12 \, \sigma$, $3 \, \pi$
- (c) 6σ , 9π
- (d) 15σ only
- **8.** When boron reacts with NH₃, compound *X* and H₂ are formed. *X* on reaction with HF gives *Y*. What are *X* and *Y* respectively?
 - (a) BN and B₂O₃
- (b) B₃N₃H₆ and NH₃
- (a) DN and NII
- (c) BN and NH₄BF₄ (d) B₃N₃H₆ and B₂O₃
- 9. Boric acid is a Lewis acid because its molecule
 - (a) contains replaceable H⁺ ion
 - (b) gives up a proton
 - (c) accepts OH⁻ from water releasing proton
 - (d) combines with proton from water molecule.

(NEET Phase-II 2016)

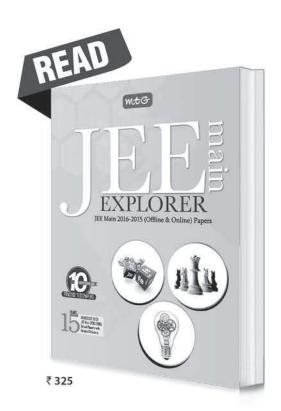
- 10. Synthesis gas is a mixture of
 - (a) steam and CO
- (b) CO and N₂
- (c) H₂ and CO
- (d) H₂ and CH₄
- 11. Which of the following acids can be used to dissolve lead (II) oxide?
 - (a) HNO₃
- (b) H₂SO₄
- (c) HCl
- (d) None of these
- 12. The stability of + 1 oxidation state among Al, Ga, In and Tl increases in the sequence
 - (a) Al < Ga < In < Tl
- (b) Tl < In < Ga < Al
- (c) In < Tl < Ga < Al
- (d) Ga < In < Al < Tl

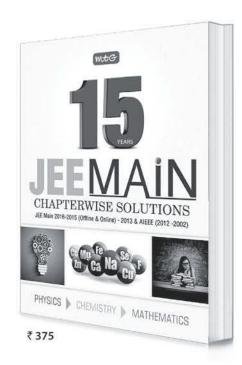
(AIPMT 2015)

- **13.** In the context of the Hall–Heroult process for the extraction of Al, which of the following statements is false?
 - (a) Al^{3+} is reduced at the cathode to form Al.
 - (b) Na₃AlF₆ serves as the electrolyte.
 - (c) CO and CO₂ are produced in this process.
 - (d) Al₂O₃ is mixed with CaF₂ which lowers the melting point of the mixture and brings conductivity. (JEE Main 2015 offline)

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- **14.** An inorganic salt 'A' is a strong reducing agent. Its hydrolysis in water gives a white turbidity (B). Aqueous solution of 'A' gives a white ppt. (C) with NaOH. 'A' reduces auric chloride to produce purple of cassius. 'A' also reduces iodine and gives chromyl chloride test. Inorganic salt 'A' is
 - (a) SnCl₄
- (b) SnCl₂
- (c) Na₂SnO₂
- (d) Sn(OH)Cl
- **15.** AlF₃ is soluble in HF only in presence of KF. It is due to the formation of
 - (a) $K_3[AlF_3H_3]$
- (b) $K_3[AlF_6]$
- (c) AlH₃
- (d) $K[AlF_3H]$

(NEET Phase-II 2016)

- **16.** Which of these is not a monomer for a high molecular mass silicone polymer?
 - (a) Me₃SiCl
- (b) PhSiCl₃
- (c) MeSiCl₃
- (d) Me₂SiCl₂ (**NEET 2013**)
- **17.** The catenation tendency of C, Si and Ge is in the order Ge < Si < C. The bond energies (in kJ mol⁻¹) of C—C, Si—Si and Ge—Ge bonds respectively are
 - (a) 167, 180, 348
- (b) 180, 167, 348
- (c) 348, 167, 180
- (d) 348, 180, 167
- 18. Carbon sub-oxide (C_3O_2)
 - (a) is a foul smelling gas
 - (b) is obtained by dehydrating malonic acid with P_2O_5
 - (c) is a linear molecule
 - (d) all the above statements are correct.
- **19.** Which one of the following statements about the zeolite is false?
 - (a) They are used as cation exchangers.
 - (b) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolite.
 - (c) They have open structure which enables them to take up small molecules.
 - (d) Zeolites are aluminosilicates having three dimensional structures.
- **20.** The correct increasing order of extent of hydrolysis in the following is
 - (a) $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$
 - (b) $CCl_4 < AlCl_3 < MgCl_2 < PCl_5 < SiCl_4$
 - (c) $AlCl_3 < MgCl_2 < CCl_4 < PCl_5 < SiCl_4$
 - (d) $SiCl_4 < MgCl_2 < AlCl_3 < PCl_5 < CCl_4$
- 21. Consider the following statements,
 - I. In diamond, each carbon atom is linked tetrahedrally to four other carbon atoms with sp^3 hybridisation.

- II. Graphite has planar hexagonal layers of carbon atoms held together by weak van der Waals' forces.
- III. Silicon exists only in diamond structure due to its tendency to form $p\pi$ - $p\pi$ bonds to itself.
- (a) Only I and II are correct
- (b) Only I is correct
- (c) Only II and III are correct
- (d) All the above statements are correct.
- 22. Which of the following oxides is strongly basic?
 - (a) Tl₂O
- (b) B_2O_3
- (c) Al_2O_3
- (d) Ga₂O₃
- 23. How many O-atoms are shared per SiO_4^{4-} tetrahedral in silicate anion of beryl mineral?
 - (a) 4
- (b) 3
- (c) 2
- (d) 1
- **24.** The tendency of BF₃, BCl₃ and BBr₃ to behave as Lewis acid decreases in the sequence
 - (a) $BF_3 > BCl_3 > BBr_3$
- (b) $BCl_3 > BF_3 > BBr_3$
- (c) $BBr_3 > BCl_3 > BF_3$
- (d) $BBr_3 > BF_3 > BCl_3$
- **25.** The stability of dihalides of Si, Ge, Sn and Pb increases steadily in the sequence
 - (a) $PbX_2 < SnX_2 < SiX_2 < GeX_2$
 - (b) $GeX_2 < SiX_2 < PbX_2 < SnX_2$
 - (c) $SiX_2 < GeX_2 < PbX_2 < SnX_2$
 - (d) $SiX_2 < GeX_2 < SnX_2 < PbX_2$
- **26.** The structure of diborane (B_2H_6) contains
 - (a) four 2c-2e bonds and two 3c-2e bonds
 - (b) two 2c-2e bonds and four 3c-2e bonds
 - (c) two 2*c*-2*e* bonds and two 3*c*-2*e* bonds
 - (d) four 2c-2e bonds and four 3c-2e bonds.
- **27.** Soldiers of Napolean army while at Alps during freezing winter suffered a serious problem because of the tin buttons of their uniforms. White metallic tin buttons got converted to grey powder. This transformation is related to
 - (a) a change in the partial pressure of oxygen in the air
 - (b) a change in the crystalline structure of tin
 - (c) an interaction with nitrogen of the air at very low temperatures
 - (d) an interaction with water vapour contained in the humid air.
- 28. Glass reacts with HF to produce
 - (a) SiF₄
- (b) Na₂SiF₆
- (c) H₂SiO₃
- (d) Na₃AlF₆

- 29. Which of the following statements is correct with respect to the property of elements in the carbon family with an increase in the atomic number?
 - (a) Atomic size decreases.
 - (b) Stability of +2 oxidation state increases.
 - (c) Metallic character decreases.
 - (d) Ionisation energy increases.
- **30.** Which is true for an element *R* present in group III of the periodic table?
 - (a) It is gas at room temperature.
 - (b) It has oxidation state of +4.
 - (c) It forms R_2O_3 .
 - (d) If forms RX_2 .

SOLUTIONS

SOLUTIONS

1. (b):
$$2Al_{(s)} + N_{2(g)} \xrightarrow{\Delta} 2AlN_{(s)}$$

$$AlN_{(s)} + 3H_2O_{(l)} \xrightarrow{(D)} Al(OH)_{3(s)} + NH_{3(g)}$$

$$(C) \qquad (D)$$

- 2. (b): The increasing order of atomic radii of group 13 elements is Ga < Al < In < Tl.
 - Atomic radius of Ga is slightly lower than that of Al due to the presence of *d*-electrons in Ga which do not shield the nucleus effectively. As a result, the electrons in Ga experience greater force of attraction.
- 3. (a): Borax is used as a buffer as it contains weak acid and its salt with strong base.

$$Na_2B_4O_7 + 7H_2O \longrightarrow 2Na[B(OH)_4] + 2H_3BO_3$$

- (c): Silicon occurs in combined state in nature as silica, SiO₂.
- (a): Silica gel absorbs moisture thus, acts as drying agent. Silicon being a semiconductor is used in transistors. Silicone is a sealant while silicates including zeolites act as ion-exchangers.
- 6. (c): Lead reacts with water to form lead salts which are poisonous. Hence, lead pipes are not suitable for drinking purpose.
- 7. (b): Borazole has six B-N, three B-H and three N—H sigma bonds and three B—N pi bonds.
- 8. (c): $2B + 2NH_3 \longrightarrow 2BN + 3H_2$ $BN + 4HF \longrightarrow NH_4BF_4$
- 9. (c): Boric acid behaves as a Lewis acid, by accepting a pair of electrons from OH ion of water thereby releasing a proton.

$$H \longrightarrow [B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$

- **10.** (c): Mixture of H₂ and CO is known as synthesis gas or water gas or syn gas.
- 11. (a): Nitric acid. This is because lead nitrate formed is soluble in water. If H₂SO₄ is used, an insoluble layer of PbSO₄ is deposited on the surface of powder and prevents the further reaction. Likewise, PbCl₂ prevents the reaction with HCl.
- 12. (a): In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect. Hence, stability of +1 oxidation state increases in the sequence : Al < Ga < In < Tl.
- 13.(b): In Hall Heroult process for the extraction of Al, electrolyte is Al₂O₃ dissolved in Na₃AlF₆ containing a little of CaF₂.

14. (b):
$$SnCl_2 + H_2O \longrightarrow Sn(OH)Cl + HCl$$

$$(A) \qquad (B)$$
 $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$

$$(C)$$
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$
 $3SnCl_2 + 2AuCl_3 \longrightarrow 3SnCl_4 + 2Au$

SnCl₄ undergoes hydrolysis forming stannic acid which absorbs colloidal particles of gold and forms purple of cassius.

$$SnCl_2 + 2HCl + I_2 \longrightarrow SnCl_4 + 2HI$$

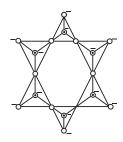
15. (b): AlF₃ is insoluble in anhydrous HF because the F ions are not available in hydrogen bonded HF but, it becomes soluble in presence of little amount of KF due to formation of complex, K₃[AlF₆]

$$AlF_3 + 3KF \longrightarrow K_3[AlF_6]$$

Soluble complex

- **16.** (a): It can form only dimer.
- 17. (d): Higher the bond energies of element-element bond, more is the catenation tendency.
- 18. (d)
- **19.** (b): Zeolites have SiO_4 and AlO_4 tetrahedrons linked together in a three dimensional open structure in which four or six membered rings predominate. Due to open chain structure they have cavities and can take up water and other small molecules.
- **20.** (a): Extent of hydrolysis increases in the order: $CCl_4 < MgCl_2 < AlCl_3 < SiCl_4 < PCl_5$
- 22.(a): As we move down the group, the basic nature of the oxides of group 13 elements increases. Tl₂O in aqueous solution gives TlOH which is a strong base as alkali metal hydroxides.

23. (c): Beryl mineral (Be₃Al₂Si₆O₁₈) is an example of cyclic silicates which are formed by sharing of two oxygen atoms per tetrahedron (SiO₄⁴⁻) units and contain $[(SiO_3^{2-})]_n$ basic unit as represented by the following structure:



Cyclic $Si_6O_{18}^{12-}$ unit in beryl O = Oxygen \bullet = Silicon

24. (c): Lewis acid character decreases in the order: $BBr_3 > BCl_3 > BF_3$

This is due to the $p\pi$ - $p\pi$ back bonding in boron

25.(d): The stability of dihalides increases in the sequence : $SiX_2 < GeX_2 < SnX_2 < PbX_2$.

$$3c - 2e : B - H - B; 2c - 2e : H - B - H$$

27. (b): Grey tin is very brittle and easily crumbles down to a powder in very cold climates.

Grey tin ← White tin (Cubic) (Tetragonal)

The change of white tin to grey tin is accompanied by increase in volume. This is called tin disease or tin plague.

- 28. (b): $Na_2SiO_3 + 6HF \longrightarrow Na_2SiF_6 + 3H_2O$ $CaSiO_3 + 6HF \longrightarrow CaSiF_6 + 3H_2O$
- 29. (b): In carbon family, stability of +2 oxidation state increases on moving down the group with an increase in atomic number due to inert pair effect.
- 30. (c): Al \rightarrow group III \rightarrow Forms Al₂O₃



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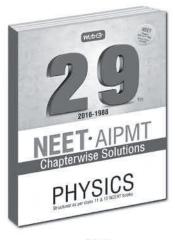
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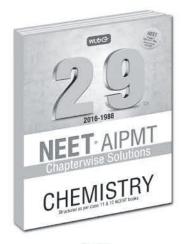


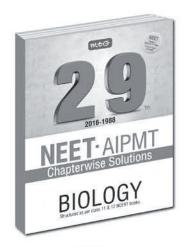
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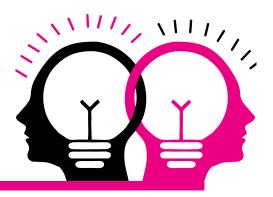
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EXAMINE



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.					
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.					
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.					
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.					
Section - V	 Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as: (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false. 					
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).					

EQUILIBRIUM

SECTION - I

Only One Option Correct Type

1. At 540 K, 0.10 moles of PCl₅ are heated in a 8 litre flask. The pressure of the equilibrium mixture is found to be 1.0 atm. K_c for the reaction is (a) 4×10^{-2} mol L⁻¹ (b) 8×10^{-2} mol L⁻¹ (c) 3×10^{-4} mol L⁻¹ (d) 2×10^2 mol L⁻¹

- **2.** Consider the reaction : $AB_{2(g)} \rightleftharpoons AB_{(g)} + B_{(g)}$. If the initial pressure of AB_2 is 500 torr and equilibrium pressure is 600 torr, the equilibrium constant, K_p for the given reaction in terms of torr is (b) 50 (c) 25
- 3. A mixture of 1.57 moles of N₂, 1.92 moles of H₂ and 8.13 moles of NH3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction, $N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)} \text{ is } 1.7 \times 10^2.$

Select the true statement.

- (a) The reaction is at equilibrium.
- (b) The reaction goes in the direction of reactants.
- (c) The reaction goes in the direction of product.
- (d) None of these.
- 4. How many moles of HCl will be required to prepare one litre of buffer solution (containing NaCN + HCl)

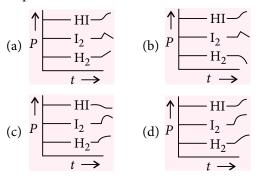
of pH 8.5 using 0.01 g formula weight of NaCN? $(K_{\text{HCN}} = 4.1 \times 10^{-10})$

- (a) 7.21×10^{-4}
- (b) 8.99×10^{-6}

- (c) 8.85×10^{-3}
- (d) 4.32×10^{-1}
- 5. If K_{sp} of AgCNS = 1×10^{-12} and K_{sp} of AgBr = 5×10^{-13} then the value of simultaneous solubility (in mol L^{-1}) of AgCNS and AgBr in water will be respectively
 - (a) 8.16×10^{-7} , 4.08×10^{-7} (b) 4.08×10^{-7} , 8.16×10^{-7}

 - (c) 8.16, 4.08
- (d) 1×10^{-12} , 5×10^{-13}
- The pH at the equivalence point of titration of 0.2 M NH₃ with 0.2 M HCl is $(pK_b \text{ of } NH_3 = 4.74)$
 - (a) 9.72
- (b) 9.87
- (c) 5.13
- (d) 4.98
- A small amount of NH₄HS is added in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH₃ and H₂S gases in the flask. When the decomposition of NH₄HS reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for the decomposition of NH₄HS at this temperature is (b) 0.18 (a) 0.30 (c) 0.17
- Consider the gaseous equilibrium of

The three gases are at equilibrium in a container as shown in the following graphs. At some time t, extra I2 is added. Which of the following sets will respond to this situation?



9. What is the correct decreasing order of strength of the following bases:

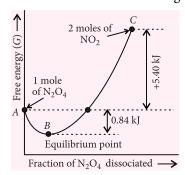
$$OH^-$$
, NH_2^- , $H-C\equiv C^-$ and $CH_3-CH_2^-$?

- (a) $CH_3 CH_2^- > NH_2^- > H C = C^- > OH^-$
- (b) $H-C \equiv C^- > CH_3 CH_2^- > NH_2^- > OH^-$
- (c) $OH^- > NH_2^- > H C \equiv C^- > CH_3 CH_2^-$
- (d) $NH_2^- > H C \equiv C^- > OH^- > CH_3 CH_2^-$
- 10. Zn salt is mixed with $(NH_4)_2S$ of molarity = 0.021 M, what amount of Zn²⁺ will remain unprecipitated in 12 mL of the solution? $[K_{sp} \text{ of ZnS} = 4.51 \times 10^{-24}]$
 - (a) 4.232×10^{-20} g
- (b) 1.677×10^{-22} g (d) 6.201×10^{-22} g
- (c) 1.999×10^{-18} g

SECTION - II

More than One Options Correct Type

11. For the dissociation equilibrium, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, the variation of free energy with the fraction of N₂O₄ dissociated under standard conditions is shown in the figure:



Which of the following statements are correct?

- (a) The free energy change for the forward reaction is negative.
- (b) The free energy change for the backward reaction is negative.

- (c) The net free energy change for the complete reaction is positive.
- (d) Forward reaction is more spontaneous than backward reaction.
- **12.** The equilibrium constant of the following reaction in equilibrium at 27°C,

$$A + B \Longrightarrow C + D$$
 is 10.

Which of the following statements for the given reaction are correct?

- (a) Free energy change of the reaction is zero.
- (b) Standard free energy of the reaction is zero.
- (c) Standard free energy of the reaction is -5.74 kJ.
- (d) Free energy change when all the reactants and products are 1 molal each will be -5.74 kJ.
- **13.** For which of the following reactions, $K_p = K_c$?
 - (a) $H_{2(g)} + I_{2(g)} \Longrightarrow 2HI_{(g)}$
 - (b) $2N_2O_{4(g)} \rightleftharpoons 4NO_{2(g)}$
 - (c) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
 - (d) $H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Whenever a salt is dissolved in water, nature of the resulting solution depends upon the extent to which either one or both the ions interact with water. To know more about such processes it would be advantageous to treat such system mathematically. A cation which is weaker acid than H₃O⁺ and has its conjugate base stronger than both OH⁻ and H₂O does not hydrolyse.

$$Na^+ + H_2O \longrightarrow NaOH + H^+$$

Na⁺ is a weaker acid than H₃O⁺ and its conjugate base NaOH is stronger than both H₂O and OH⁻ hence, Na⁺ does not hydrolyse.

- **14.** Which of the following shows cationic hydrolysis?
 - (a) Na⁺
- (b) K⁺
- (c) Ba²⁺
- (d) None of these
- 15. Which of the following gives acidic solution due to cationic hydrolysis?
 - (a) NaCN
- (b) KCl
- (c) NH₄Cl
- (d) BaS

Paragraph for Questions 16 and 17

Physical and chemical equilibria respond to stress, e.g., change in pressure, temperature and concentration of reactants and products. According to Le Chatelier's principle a system at equilibrium, when subjected to a disturbance (stress), responds in a way that tends to minimize the effect of the disturbance.

16. Consider the equilibrium,

$$2CO_{(g)} + O_{2(g)} \Longrightarrow 2CO_{2(g)} + Heat$$

If O₂ is added and volume of the reaction vessel is reduced, the equilibrium will

- (a) shift in forward direction
- (b) shift in reverse direction
- (c) remain unchanged
- (d) be unpredictable.
- 17. Manufacture of lime from limestone as:

 $CaCO_{3(s)} + Heat \longrightarrow CaO_{(s)} + CO_{2(g)}$ is most favoured by

- (a) heating limestone in a closed container
- (b) heating limestone in an open container
- (c) adding more limestone to the reaction container
- (d) decreasing the temperature.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists:

Given:
$$A_2 + B_2 \longrightarrow C$$
; $K = 4$
 $C + 2B_2 \longrightarrow 2D_2$; $K = 16$

K = 4

List I

List II

(Reactions)

(Equilibrium constant)

$$(P) \ \frac{1}{2}A_2 + \frac{3}{2}B_2 \longrightarrow D_2$$

1.
$$\frac{1}{4}$$

$$(Q) 2D_2 \longrightarrow A_2 + 3B_2$$

$$(R) A_2 + 3B_2 \longrightarrow 2D_2$$

(S)
$$D_2 \longrightarrow B_2 + \frac{1}{2}C$$

Q R

- (a) 1
- (b) 1 3
- (c) 4 3
- (d) 4
- 19. Match the List I with List II and select the correct answer using the codes given below the lists:

List I

- (P) Degree of hydrolysis for salts of strong acid and weak base
- (Q) Hydrolysis constant

List II

- 1. the hydrolysis of anion which irreversible.
- 2. is not possible because of the reaction of strong base with strong acid.

- (R) Na₂O in water is 3. is affected basic due to
- temperature and concentration is changed.

(S)
$$Na^+ + H_2O \rightleftharpoons$$
 $NaOH + H^+$

is independent of volume of solution taken but depends upon temperature.

P Q R S

- (a) 4
- (b) 3 2
- 2 (c) 1 4
- (d) 2 1 3 4

SECTION - V

Assertion Reason Type

20. Assertion: In the qualitative analysis of third group, NH₄Cl is added to NH₄OH medium.

Reason: This is to convert the ions of group into their respective chlorides.

21. Assertion: Aqueous solution of ammonium carbonate is basic.

Reason: Acidic/basic nature of a salt of weak acid and weak base depends on K_a and K_b values of the acid and the base forming it.

22. Assertion: Quicklime dissolves more in hot water than in water at room temperature.

Reason: Dissolution of quicklime in water is endothermic.

SECTION - VI

Integer Value Correct Type

- 23. The pH at the equivalence point for the titration of 0.10 M KH₂BO₃ with 0.1 M HCl is (x + 0.22). The value of *x* is $(K_a \text{ for H}_3 BO_3 = 7.2 \times 10^{-10})$
- 24. 0.01 M AgBr is gradually added to a solution that has $[CrO_4^{2-}] = 0.010 \text{ M}$ and $[Br^{-}] = 0.010 \text{ M}$. [Br⁻] remaining in the solution at the point where Ag_2CrO_4 starts precipitating is 3.33×10^{-x} M. The value of x is

 $K_{sp}(Ag_2CrO_4) = 2.25 \times 10^{-12}, K_{sp}(AgBr) = 5.0 \times 10^{-13}$

25. Ionisation constant of formic acid is 2×10^{-4} at 198 K. The H₃O⁺ ion concentration in 0.01 M solution of formic acid is 1.4×10^{-x} mol L⁻¹. The value of x is

THE p-BLOCK ELEMENTS

SECTION - I

Only One Option Correct Type

- 1. When Sn is treated with conc. HNO₃
 - (a) it is converted into stannous nitrate
 - (b) it is converted into stannic nitrate
 - (c) it is converted into metastannic acid
 - (d) it becomes passive.
- **2.** Sodium hydride reacts with diborane in *Y* to give a tetrahedral compound '*Z*' which is extensively used as reducing agent in organic synthesis. The *Y* and *Z* in the above reaction are respectively
 - (a) C₂H₆, C₂H₅ONa
 - (b) C_2H_5 —O— C_2H_5 , $NaBH_4$
 - (c) NH₃, B₃N₃H₆
 - (d) C_3H_8 , C_2H_6ONa
- **3.** Fluorine is more electronegative than either boron or phosphorus. What conclusion can be drawn from the fact that BF₃ has no dipole moment but PF₃ does?
 - (a) BF₃ is not spherically symmetrical but PF₃ is spherically symmetrical.
 - (b) BF₃ molecule must be linear.
 - (c) The atomic radius of P is larger than that of B.
 - (d) The BF₃ molecule must be triangular planar.
- **4.** A certain salt (*X*) gives the following tests :
 - (i) Its aqueous solution is alkaline to litmus test.
 - (ii) On strongly heating it swells to give a glassy bead.
 - (iii) When concentrated sulphuric acid is added to a hot concentrated solution of (X), crystals of monobasic Lewis acid of boron (Y) separate out. Identify the colour of crystals (Y).
 - (a) White
- (b) Blue
- (c) Brown
- (d) Violet
- 5. In phosgene,
 - (a) C—O bond length is longer while C—Cl bond length is shorter than expected
 - (b) C—O bond length is shorter while C—Cl bond length is longer than expected
 - (c) all C—O and C—Cl bond lengths are equal
 - (d) the values of C—O and C—Cl bond lengths are the same as expected.
- **6.** $Pb(NO_3)_2$ on heating gives
 - (a) NO
- (b) N_2O_3
- (c) a residue of PbO
- (d) none of these.

- 7. Which of the following statements is correct?
 - (a) Coke is found in nature.
 - (b) Producer gas is a mixture of CO and H₂.
 - (c) CO is used in the extraction of Ni by Mond's process.
 - (d) CO₂ can be prepared by dehydration of formic acid.
- 8. PbCl₄ exists but PbBr₄ and PbI₄ do not, because
 - (a) of inability of bromine and iodine to oxidise Pb²⁺to Pb⁴⁺
 - (b) Br and I ions are bigger in size
 - (c) of more electropositive nature of bromine and iodine
 - (d) chlorine is a gas.
- 9. Alum helps in purifying water by
 - (a) forming Si complex with clay particles
 - (b) sulphate part which combines with the dirt and removes it.
 - (c) coagulating the mud particles
 - (d) making mud particles soluble.
- **10.** H_3BO_3 is
 - (a) monobasic and weak Lewis acid
 - (b) monobasic and weak Bronsted acid
 - (c) monobasic and strong Lewis acid
 - (d) tribasic and weak Bronsted acid.

SECTION - II

More than One Options Correct Type

- 11. Which of the following statements are incorrect?
 - (a) AlCl₃ exists as Al₂Cl₆ in vapour state.
 - (b) All the Al—Cl bonds in Al₂Cl₆ are equivalent.
 - (c) Borax when heated with ammonium chloride forms ammonium tetraborate.
 - (d) AlF₃ is a high m.pt. solid while AlCl₃ is a low m.pt. volatile solid.
- **12.** On heating with carbon which of the following elements do not form carbides?
 - (a) In
- (b) Ga
- (c) B
- (d) Al
- **13.** Me₃SiCl is used during polymerisation of organo silicones because
 - (a) the chain length of organosilicon polymers can be controlled by adding Me₃SiCl
 - (b) Me₃SiCl blocks the terminal of silicon polymer
 - (c) Me₃SiCl improves the quality and yield of the polymer
 - (d) Me₃SiCl acts as a catalyst during polymerisation.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

All the elements of group 14 except Pb show allotropy. Carbon exists in several microcrystalline forms which were originally regarded as amorphous form. It also exists in three crystalline allotropic forms (diamond, graphite and fullerenes). Silicon also exists in crystalline and amorphous forms. Germanium exists in two crystalline forms while tin exists in three forms called grey, white and rhombic tin.

- 14. Carbon atoms in diamond are arranged in
 - (a) planar configuration
 - (b) tetrahedral configuration
 - (c) linear configuration
 - (d) octahedral configuration.
- 15. Most impure form of carbon is
 - (a) animal charcoal
- (b) lamp black
- (c) graphite
- (d) wood charcoal.

Paragraph for Questions 16 and 17

The heavier elements of group 13 and 14 besides their group oxidation state exhibit another oxidation state which is two units lower than the group oxidation state. The stability of lower oxidation state increases on moving down the group due to inert pair effect.

- **16.** Which of the following statements is incorrect?
 - (a) Boron exhibits +3 oxidation state only.
 - (b) In Ga, +3 oxidation state is more stable than +1 oxidation state.
 - (c) In Sn, +2 oxidation state is more stable than +4 oxidation state.
 - (d) In Tl, +1 oxidation state is more stable than +3 oxidation state.
- **17.** The strongest oxidising agent among the given compounds is
 - (a) SiO₂
- (b) GeO₂
- (c) SnO₂
- (d) PbO₂

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists:

List	

- List II
- (P) B₄C
- 1. Highly toxic
- (Q) AlCl₃
- 2. Quartz thermostats
- (R) Ga
- 3. Bullet proof clothing
- (S) Tl
- 4. Catalyst

- P Q R S
- (a) 4 1 3 2
- (b) 2 3 4 1
- (c) 1 2 3 4
- (d) 3 4 2 1
- **19.** Match the List I with List II and select the correct answer using the codes given below the lists:

List I

List II

- (P) Borazine
- 1. Na₂SiO₃
- (Q) Phosgene
- 2. Bead with copper salts
- (R) Water glass
- 3. COCl₂
- (S) Borax
- 4. $B_3N_3H_6$
- P Q R S
- (a) 4 1 2 3
- (b) 3 4 2
- (c) 1 2 3 4
- (d) 4
- 3 1 2

1

SECTION - V

Assertion Reason Type

- **20. Assertion**: Between SiCl₄ and CCl₄, only SiCl₄ reacts with water.
 - **Reason**: SiCl₄ is ionic and CCl₄ is covalent.
- **21. Assertion :** Trisilylamine is a relatively weaker base as compared to trimethylamine.
 - **Reason :** In trisilylamine, N atom is sp^2 -hybridised and lone pair on N is involved in back π -bonding.
- **22. Assertion** : Calcium carbide on hydrolysis gives acetylene.

Reason: Calcium carbide contains C⁴⁻ anions.

SECTION - VI

Integer Value Correct Type

- **23.** The number of water molecules present in butter of tin is
- **24.** The following structure is a silicate having formula $Si_3O_9^{x-}$. The value of x is



25. Amongst the following, the maximum number of compounds showing covalent nature is BCl₃, BBr₃, AlF₃, AlCl₃, AlBr₃, Al(NO₃)₃, Al₂(SO₄)₃

EQUILIBRIUM

- 1. (a)
- 3. **(b)**: $N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)}$ $Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$
 - Given, $[NH_3] = \frac{8.13}{20} M = 0.4065 M;$

$$[N_2] = \frac{1.57}{20} M = 0.0785 M$$

$$[H_2] = \frac{1.92}{20} M = 0.096 M$$

$$Q_c = \frac{[0.4065 \text{ M}]^2}{[0.0785 \text{ M}][0.096 \text{ M}]^3} = 2.379 \times 10^3 \text{ M}^{-2}$$

- $Q_c \neq K_c$, so the reaction is not in equilibrium. $Q_c > K_c$, it indicates that the reaction will proceed in the direction of reactants.
- 4. (c): (NaCN + HCl) is a conditional buffer and it will behave as buffer only if HCl is in lesser amount than NaCN. In this condition, mixture of (NaCN + HCN) will act as acidic buffer.

Let *x* mole of HCl be used.

 $NaCN + HCl \rightarrow NaCl + HCN$ Mole taken initially 0.01

Mole after reaction (0.01 - x)x

$$\therefore pH = -\log K_a + \log \left(\frac{0.01 - x}{x} \right)$$

$$8.5 = -\log(4.1 \times 10^{-10}) + \log\left(\frac{0.01 - x}{x}\right)$$

- $x = 8.85 \times 10^{-3} \text{ mole}$
- 5. (a): Let the solubilities of AgCNS and AgBr in water be *x* and *y* respectively.

$$AgCNS \rightleftharpoons Ag^+ + CNS$$

$$AgBr \rightleftharpoons Ag^{+} + Br^{-}$$

water be x and y respectively.

$$AgCNS \rightleftharpoons Ag^{+} + CNS^{-}$$

$$x \qquad x$$

$$AgBr \rightleftharpoons Ag^{+} + Br^{-}$$

$$y \qquad y$$

$$\therefore [Ag^{+}] = (x + y), [CNS^{-}] = x, [Br^{-}] = y$$

$$K_{-}[A_{+}CNS] = (A_{+}^{+}[A_{+}CNS^{-}], (x + x) = 0$$

$$K_{sp}[AgCNS] = [Ag^{+}][CNS^{-}] = (x + y)x$$

$$\Rightarrow 1 \times 10^{-12} = (x + y)x \qquad ...(i)$$

and
$$K_{sp}[AgBr] = [Ag^+][Br^-] = (x + y)y$$

$$\Rightarrow 5 \times 10^{-13} = (x + y)y \qquad ...(ii)$$

On solving eq. (i) and (ii), we get

$$x = 8.16 \times 10^{-7} \text{ mol/L}$$

 $y = 4.08 \times 10^{-7} \text{ mol/L}$

$$v = 4.08 \times 10^{-7} \text{ mol/L}$$

- (c): $NH_3 + HCl \rightarrow NH_4Cl$
 - At the equivalence point, the volume of resulting solution is doubled.

Hence,
$$[NH_4Cl] = \frac{0.2}{2} = 0.1 \text{ M}$$

$$: [NH_4^+] = 0.1 \text{ M}$$

The salt hydrolyses,

$$pH = \frac{1}{2}(pK_w - pK_b - \log[NH_4^+])$$

$$=\frac{1}{2}(14-4.74-\log 0.1)=5.13$$

 $NH_4HS_{(s)} \Longrightarrow NH_{3(g)} + H_2S_{(g)}$ 7. (d): Initial a moles

At. eqm. (a - x) moles (0.5 + p) atm p atm.

i.e., if x moles of NH_4HS decompose, Increase in pressure due to NH₃

= Increase in pressure due to H₂S

Let it be *p* atm.

Total pressure at equilibrium = 0.5 + p + p= 0.5 + 2p atm

$$0.5 + 2p = 0.84$$
 atm or $p = 0.17$ atm

$$p_{\text{NH}} = 0.5 + 0.17 = 0.67 \text{ atm}$$

$$p_{\rm H, S}^{\rm NH_3} = 0.17 \text{ atm}$$

$$p_{NH_3} = 0.5 + 0.17 = 0.67 \text{ atm}$$

$$p_{H_2S} = 0.17 \text{ atm}$$

$$K_p = p_{NH_3} \times p_{H_2S} = 0.67 \text{ atm} \times 0.17 \text{ atm}$$

$$= 0.1139 \text{ atm}^2$$

8. (b):
$$K_p = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} \times p_{\text{I}_2}}$$

- When I₂ is added at equilibrium, the reaction moves in a direction where its concentration is reduced, i.e., in the forward direction (Le-Chatelier's Principle). Thus, concentration of HI increases whereas that of H₂ decreases. When I₂ is added initially its concentration increases, but gradually it decreases as the reaction proceeds.
- (a)
- **10. (b)**: $(NH_4)_2S = 0.021 M$;

$$[S^{2-}] = 0.021 \text{ M}$$

 $[S^{2^{-}}] = 0.021 \text{ M}$ At equilibrium, $[Zn^{2^{+}}][S^{2^{-}}] = K_{sp}$ of ZnS

$$[Zn^{2+}] = \frac{4.51 \times 10^{-24}}{0.021} = 2.15 \times 10^{-22} M$$

 $[Zn^{2+}]$ left in solution = $2.15 \times 10^{-22} \times 65$ g/litre

$$= \frac{2.15 \times 10^{-22} \times 65 \times 12}{1000} \,\mathrm{g/12} \;\mathrm{mL}$$

$$= 1.677 \times 10^{-22} \text{ g/12 mL}$$

11. (a, b, c): ΔG° for conversion of 1 mole of N₂O₄ into equilibrium mixture (forward reaction)

$$= -0.84$$
 kJ, *i.e.*, $-ve$

 ΔG° for conversion of 2 moles of NO₂ into equilibrium mixture (backward reaction)

$$= -5.40 + (-0.84) = -6.24$$
 kJ, *i.e.*, -ve

 ΔG° for conversion of 1 mole of N₂O₄ completely into 2 moles of NO₂ = +5.40 kJ.

 ΔG° for complete conversion is positive therefore, complete conversion is not possible.

As ΔG° for backward reaction is more negative than for forward reaction, *i.e.*, formation of N₂O₄ is more spontaneous.

12. (a, c, d): (a) For a system to be in equilibrium, $\Delta G = 0$ (c) $\Delta G^{\circ} = -2.303 \ RT \log K$

=
$$-2.303 \times 8.314 \times 300 \times \log 10 = -5.74 \text{ kJ}$$
 (d) ΔG° is the free energy change when all the reactants having unit concentrations change into

reactants having unit concentrations change into the products having unit concentrations.

- 13. (a, d) 14. (c)
- 15. (c): NH₄Cl is a salt of weak base and strong acid.
- **16.** (a): Addition of O₂ will cause the equilibrium to shift in forward direction because that way it is consumed. Reduction in volume *i.e.*, increase in pressure also causes the equilibrium to shift in forward direction leading to smaller number of moles of gases.
- 17. (b): In an open container, CO_2 formed in the reaction, $CaCO_{3(g)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, passes into atmosphere and equilibrium continues to shift in forward direction leading to the completion of the reaction.
- 18. (d) 19. (b)
- **20.** (c): NH₄Cl suppresses the ionisation of NH₄OH due to common ion effect and concentration of OH $^-$ ions is just sufficient to precipitate third group radicals as hydroxides. Group IV hydroxides, having high K_{sp} , are not precipitated.
- 21. (a): $(NH_4)_2CO_3 \rightarrow 2NH_4^+ + CO_3^{2-}$ $2H_2O \rightarrow 2OH^- + 2H^+$ $\downarrow \qquad \qquad \downarrow$ $NH_4OH + H_2CO_3$ Weak base Weak acid

 $[K_h \text{ of } NH_4OH > K_a \text{ of } H_2CO_3]$

22. (d): Quicklime dissolves less at higher temperature because dissolution is exothermic.

23. (5): $KH_2BO_3 + HCl \rightarrow H_3BO_3 + KCl$

At the equivalence point, the concentration of $H_3BO_3 = 0.05 \text{ M}$

 H_3BO_3 then ionises, thus, the equilibrium established in aqueous solution of H_3BO_3

$$H_3BO_3 + H_2O \Longrightarrow B(OH)_4^- + H^+$$

$$K_a = \frac{[H^+][B(OH)_4^-]}{[H_3BO_3]}$$

$$7.2 \times 10^{-10} = \frac{x^2}{0.05} \implies x = 0.6 \times 10^{-5}$$

- \therefore [H⁺] = 6 × 10⁻⁶ M or pH = 5.22 = (5 + 0.22)
- $\therefore x = 5$
- **24. (8)**: Calculate [Ag⁺], needed separately to precipitate CrO₄²⁻ and Br⁻ as Ag₂CrO₄ and AgBr respectively. Smaller the value of [Ag⁺], earlier the precipitation of that species. Using [Ag⁺] required to precipitate the ion at later stage, concentration of the ion earlier precipitated can be calculated.

For precipitation of Ag₂CrO₄, $[Ag^+]^2[CrO_4^{2-}] > K_{sp}$

$$[Ag^{+}]_{\min} = \left(\frac{K_{sp} (Ag_{2}CrO_{4})}{[CrO_{4}^{2-}]}\right)^{\frac{1}{2}} = \left(\frac{2.25 \times 10^{-12}}{0.010}\right)^{\frac{1}{2}}$$

$$= 1.50 \times 10^{-5} \text{ M}$$

For the precipitation of AgBr, $[Ag^+][Br^-] > K_{sp}$

$$[Ag^{+}]_{min} = \frac{K_{sp}(AgBr)}{[Br^{-}]} = \frac{5.0 \times 10^{-13}}{0.010} = 5.0 \times 10^{-11} M$$

[Ag⁺] required for precipitation of AgBr is less than that required for precipitation of Ag₂CrO₄. Hence, AgBr precipitates earlier than Ag₂CrO₄.

[Ag⁺] when Ag₂CrO₄ starts precipitating

$$= 1.50 \times 10^{-5} \text{ M}$$

[Br⁻] remaining at this stage

$$= \frac{K_{sp}(AgBr)}{[Ag^+]} = \frac{5.0 \times 10^{-13}}{1.5 \times 10^{-5}} = 3.33 \times 10^{-8} M$$

25. (3): $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$

$$K_a = \frac{[\text{HCOO}^-][\text{H}_3\text{O}^+]}{[\text{HCOOH}]} = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HCOOH}]}$$

$$2 \times 10^{-4} = \frac{[\text{H}_3\text{O}^+]^2}{0.01}$$
 or $[\text{H}_3\text{O}^+]^2 = 2 \times 10^{-6}$

or
$$[H_3O^+] = 1.4 \times 10^{-3} \text{ mol L}^{-1}$$

THE p-BLOCK ELEMENTS

- 1. (c): $Sn + 4HNO_3 \rightarrow H_2SnO_3 + 4NO_2 + H_2O$ Metastannic acid
- 2. **(b)**: $2\text{NaH} + \text{B}_2\text{H}_6 \xrightarrow{\text{C}_2\text{H}_5-\text{O}-\text{C}_2\text{H}_5(Y)} 2\text{NaBH}_4$
- **3.** (d): BF₃ is triangular planar while PF₃ is pyramidal.
- **4.** (a): (X) is borax, $Na_2B_4O_7 \cdot 10H_2O$
 - (i) $Na_2B_4O_7 + 7H_2O \Longrightarrow 2NaOH + 4H_3BO_3$ Strong Weak Base Acid

Due to presence of NaOH, the aqueous solution is alkaline to litmus.

(ii)
$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{Heat} Na_2B_4O_7 \downarrow \Delta$$

$$2NaBO_2 + B_2O_3$$
Glassy bead

(iii) Na
$$_2$$
B $_4$ O $_7$ + H $_2$ SO $_4$ + 5H $_2$ O \longrightarrow Na $_2$ SO $_4$ + 4H $_3$ BO $_3$ White crystals (Y)

- 5. (a)
- 6. (c): $2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 \uparrow + O_2 \uparrow$
- (c): Coke is not found in nature. It is an artificial
 product. Producer gas is a mixture of CO and N₂.
 CO₂ cannot be formed by dehydration of formic
 acid.

$$\text{HCOOH} \xrightarrow{\text{Conc.}} \text{CO} + \text{H}_2\text{O}$$

- **8.** (a): Bromine and iodine are weaker oxidising agents and hence cannot oxidise Pb²⁺ to Pb⁴⁺ ions.
- 9. (c): Alum is used to purify water by neutralising the electrical double layer surrounding very fine suspended particles, allowing them to coagulate. After coagulation, the particles will be large enough to settle and thus, can be removed.
- 10. (a) 11. (b, c)
- **12.** (a, b): On heating with carbon, In and Ga do not form carbides.
- 13. (a, b): Because of the presence of only one —OH group in the hydrolysis product of Me₃SiCl, it blocks the terminal of silicon polymer thus, control the chain length.
- 14. (b)

- **15.** (d): Wood charcoal is the most impure form of carbon.
- 16. (c)
- 17. (d): For Pb the more stable oxidation state is +2 but in PbO₂, it is in +4 oxidation state thus PbO₂ has great tendency to get reduced into PbO (+2 O.S.). Therefore, it acts as an strong oxidising agent.
- 18. (d): Fibres of B₄C are used to make bullet-proof clothing, AlCl₃ is used as Lewis acid catalyst, Ga remains liquid over a wide range of temperature (303 K to 2510 K). It has been used in quartz thermostats for measuring high temperatures. Tl metal is highly toxic.
- 19. (d): (P) \rightarrow 4; Borazine is $B_3N_3H_6$
 - $(Q) \rightarrow 3$; Phosgene is $COCl_2$
 - (R) \rightarrow 1; Water glass is Na₂SiO₃
 - (S) \rightarrow 2; Borax gives beads of characteristic colour with copper salts on heating.
- 20. (c): SiCl₄ undergoes hydrolysis due to the presence of empty *d*-orbitals in the valence shell of Si, while C has no available *d* orbitals to accommodate electron pairs donated by water molecules during hydrolysis.
- **21.** (a): Trisilylamine is a relatively weaker base as compared to trimethylamine.
- **22.** (c): Calcium carbide on hydrolysis gives acetylene. Calcium carbide contains C_2^{2-} anions.
- 23. (5): The molecular formula of butter of tin is $SnCl_4 \cdot 5H_2O$ in which the number of water molecules is 5.
- **24.** (6): $Si_3O_9^{6-}$
- **25.** (**4**): BCl₃, BBr₃, AlCl₃ and AlBr₃ are covalent compounds.

									~ ~
	MPP-6	CL/	ASS XII			ANSW	ER	KEY	1
1.	(b)	2.	(c)	3.	(d)	4.	(c)	5.	(a)
6.	(c)	7.	(a)	8.	(d)	9.	(c)	10.	(a)
11.	(a)	12.	(c)	13.	(b)	14.	(c)	15.	(a)
16.	(a)	17.	(b)	18.	(a)	19.	(c)	20.	(a,b)
21.	(a,b,c)	22.	(a,c)	23.	(a,c	24.	(3)	25.	(5)
26.	(4)	27.	(d)	28.	(d)	29.	(a)	30.	(b)

VITEEE-2017

B.Tech Engineering Entrance Exam Application forms sales begins



VIT University Chancellor Dr.G.Viswanathan inaugurating the sale of application forms for the VIT University Entrance Examinations (VITEEE-2017) at the Head Post Office, Vellore. Also VIT Vice Presidents Dr. Sekar Viswanathan, Mr. G.V. Selvam, Pro-Vice Chancellors Dr. V. Raju, Dr. S. Narayanan, Mr. L. Chandrasekaran, Superintendent of Postal Services, Vellore Division, Mr. N. Murali, Asst. Supdt. of Postal Services, Mr.Selvakumar, Marketing Executive and Dr. K. Manivannan, Director-UG Admissions, VIT, were present.

The sale of application forms for the VIT University Entrance Examinations (VITEEE-2017) to be held in April next year, for B.Tech courses various streams, began in all the 42 Head Post Offices, with the VIT University Chancellor Dr.G.Viswanathan inaugurating it at the Head Post Office, here, on Wednesday.

Also VIT Vice Presidents Dr. Sekar Viswanathan, Mr. G.V. Selvam, Pro-Vice Chancellors Dr. V. Raju, Dr. S. Narayanan, Mr. L. Chandrasekaran, Superintendent of Postal Services, Vellore Division, Ms. T. Sheeba Selvamani, Senior Postmaster, Vellore Head Post Office, Mr.N. Murali, Asst. Supdt. of Postal Services, Mr.Selvakumar, Marketing Executive, Postal Service, Vellore Division and Dr. K. Manivannan, Director-UG Admissions, VIT, were present. It is scheduled that the entrance examinations for the B.Tech offered in the VIT University, Vellore, Chennai, Amaravati, AP and Bhopal Campuses, will be held from **April 5th to April 16th 2017**. This Computer Based Test (CBT) is held in **119 cities including Dubai, Kuwait and Muscat**.

The University offers courses in **Vellore Campus** - Bio-Medical Engineering, Biotechnology, Computer Science and Engineering (Specialisation in Bioinformatics), Civil Engineering, Chemical Engineering, Computer Science and Engineering, Electronics and Communication Engineering, Electrical and Electronics Engineering, Electronics and Instrumentation Engineering, Information Technology, Mechanical Engineering, Mechanical (Specialisation in Automotive Engineering), Mechanical Engineering (Specialisation in Energy Engineering), Production and Industrial Engineering.

Chennai Campus – B.Tech in Civil Engineering, Computer Science and Engineering, Electronics and Communication Engineering, Electrical and Electronics Engineering, Mechanical Engineering, Electronics and Computer Engineering and Fashion Technology.

Amaravati, AP Campus – B.Tech. in Mechanical Engineering, Electronics and Communication Engineering, Computer Science Engineering, Computer Science Engineering (Specialication in Data Analytics), Computer Science Engineering (Specialication in Network and Security) and Electrical and Electronics Engineering.

Bhopal Campus – B. Tech. in Computer Science Engineering, Electronics and Communication Engineering and Electronics and Computer Engineering.

The entrance examination application forms from the Head Post Offices it can be obtained by sending a Demand Draft for Rs. 990/- drawn in favour of VIT University, payable at Vellore to the Director — UG Admissions or by cash payment at selected post offices across the country. Issuing of online and offline application has commenced from November 9th 2016.

Candidates can also apply online at www.vit.ac.in (online applicants need to pay Rs. 970/- only). The last date for applying is 28th February, 2017.

VIT University has been consistently been ranked among the premier engineering institutions of the country by India Today. VIT has an impressive track record of placement.

Visit: www.vit.ac.in for further details.





The *p*-Block Elements Organic Chemistry - Some Basic Principles and Techniques

Time Allowed: 3 hours Maximum Marks: 70

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- Write balanced equation for the preparation of elemental boron by reduction of BBr₃ with dihydrogen.
- 2. Give the IUPAC name for the following amine:

- 3. Why is B—X bond distance in B X_3 shorter than the theoretically expected value?
- **4.** What type of structural isomerism is shown by $CH_3-S-CH_2CH_2CH_3$ and $CH_3-S-CH(CH_3)_2$?
- **5.** What is inert pair effect?
- 6. Why does SO₃ act as an electrophile?
- 7. Give reason for the following:
 - (i) Conc. HNO₃ can be stored in aluminium container.
 - (ii) A mixture of dilute NaOH and aluminium pieces is used to open drain.

 Write the resonating structures of CH₂=CH-CHO. Indicate the relative decreasing order of stability of the contributing resonating structures.

OR

- 0.2475 g of an organic compound on combustion forms 0.4950 g of carbon dioxide and 0.2025 g of water. Calculate the percentage of carbon and hydrogen in it.
- 9. A compound 'A' of boron reacts with NMe₃ to give an adduct 'B' which on hydrolysis gives a compound 'C' and hydrogen gas. Compound 'C' is an acid. Identify the compounds 'A', 'B' and 'C'. Give the reactions involved.
- 10. In Dumas method for estimation of nitrogen, 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300 K = 15 mm).

- 11. What happens when
 - (i) borax is heated strongly
 - (ii) boric acid is added to water
 - (iii) aluminium is treated with HCl?
- **12.** (i) Which bond is more polar in the following pairs of molecules?
 - (a) H₃C-H or H₃C-Br
 - (b) H_3C-NH_2 or H_3C-OH
 - (ii) Give one method for industrial preparation and one for laboratory preparation of CO and CO₂ each.
- **13.** Why does water carried through lead pipes become poisonous?
- **14.** 0.12 g of an organic compound containing phosphorus gave 0.22 g of Mg₂P₂O₇ by the usual analysis. Calculate the percentage of phosphorus in the compound.
- **15.** Explain the following:
 - (i) Gallium has higher ionisation enthalpy than aluminium.
 - (ii) Boron does not exist as B^{3+} ion.
 - (iii) Aluminium forms $[AlF_6]^{3-}$ ion but boron does not form $[BF_6]^{3-}$ ion.
- **16.** Give three points of differences between inductive effect and resonance effect.
- **17.** Identify the compounds *A*, *X* and *Z* in the following reactions.
 - (i) $A + 2HCl + 5H_2O \longrightarrow 2NaCl + X$
 - (ii) $X \xrightarrow{\Delta} \text{HBO}_2 \xrightarrow{>370 \text{ K}} Z$

OR

When BCl_3 is treated with water, it hydrolyses and forms $[B(OH)_4]^-$ only whereas $AlCl_3$ in acidified aqueous solution forms $[Al(H_2O)_6]^{3+}$ ion. Explain the hybridisation of boron and aluminium in these species.

- 18. Write the structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.
- 19. Suggest a method to purify
 - (i) camphor containing traces of common salt.
 - (ii) kerosene oil containing water.
 - (iii) a liquid which decomposes at its boiling point.

- **20.** Account for the following.
 - (i) CO is used in the extraction of metals.
 - (ii) CO is poisonous.
 - (iii) CO₂ is used in refrigeration.
- **21.** Which of the following carbocations is more stable and why?
 - (i) (CH₃)₃C⁺
- (ii) $(CD_3)_3C^+$
- 22. What happens when borax is heated on a platinum wire loop and to the resulting transparent mass, a minute amount of CuO is added and the mixture is again heated first in the oxidising flame and then in the reducing flame of a bunsen burner? Give equations.
- 23. Rahul got very upset when he came to know that his father is alcoholic (takes alcohol). As he knew about the side effects of alcohol so he wanted to keep his father away from it. He spoke to his father regarding the harmful effects of alcohol. He also discussed how alcohol affects the family and social life of an individual.
 - (i) What is the main constituent of alcoholic beverages?
 - (ii) Write the IUPAC name and hybridisation of carbons of this main constituent.
 - (iii) What are the side effects of alcoholic beverages?
 - (iv) What values are possessed by Rahul?
- **24.** (i) When aqueous solution of borax is acidified with hydrochloric acid, a white crystalline solid is formed which is soapy to touch. Is this solid acidic or basic in nature? Explain.
 - (ii) Explain the following:
 - (a) Aluminium trifluoride is insoluble in anhydrous HF but dissolves on addition of NaF.
 - (b) Aluminium trifluoride precipitates out of the resulting solution when gaseous BF₃ is bubbled through the above solution.

OR

(i) Complete the following chemical equations:

$$Z + 3\text{LiAlH}_4 \longrightarrow X + 3\text{LiF} + 3\text{AlF}_3$$

$$X + 6H_2O \longrightarrow Y + 6H_2$$

$$X + 3O_2 \xrightarrow{\Delta} B_2O_3 + 3H_2O$$

- (ii) Explain the following:
 - (a) CO_2 is a gas whereas SiO_2 is solid.
 - (b) Silicon forms SiF_6^{2-} ion whereas corresponding fluoro compound of carbon is not known.

- 25. (a) 0.35 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 mL of M/10 H₂SO₄. The excess acid required 154 mL of M/10 NaOH for neutralisation. Calculate the percentage of nitrogen in the
 - (b) Why is the carbocation F_3C^+ more stable than carbocation F_3C-C^+ . Explain.

- (a) An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.
- (b) Benzoic acid is an organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable?
- Explain the following reactions:
 - (a) Silicon is heated with methyl chloride at high temperature in the presence of copper.
 - (b) Silicon dioxide is treated with hydrogen fluoride.
 - (c) CO is heated with ZnO.
 - (ii) When metal 'X' is treated with sodium hydroxide, a white precipitate 'A' is obtained, which is soluble in excess of NaOH to give soluble complex 'B'. Compound 'A' is soluble in dilute HCl to form compound 'C'. The compound 'A' when heated strongly gives 'D', which is used to extract metal. Identify 'X', 'A', 'B', 'C' and 'D'. Write suitable equations to support their identities.

- (i) Rationalise the given statements and give chemical reactions.
 - (a) Lead (II) chloride reacts with Cl₂ to give
 - (b) Lead (IV) chloride is highly unstable towards heat.
 - (c) Lead is known not to form an iodide, PbI₄.

- (ii) Give reasons for the following:
 - (a) CCl₄ is immiscible in water, whereas SiCl₄ is easily hydrolysed.
 - (b) Carbon has a strong tendency for catenation compared to silicon.

SOLUTIONS

- 1. $2BBr_3 + 3H_2 \longrightarrow 2B + 6HBr$
- CH₃-N--CH-CH₂CH₃ | | CH₃ C₂H₅

IUPAC name: 3-(N,N-Dimethyl)-3-pentanamine.

- This is due to $p\pi$ - $p\pi$ back bonding of the fully filled p-orbital of halogen (X) into the empty p-orbital of boron.
- 4. Metamerism
- 5. In the elements of 4th, 5th and 6th period of the p-block, ns²-electrons remain more tightly held by the nucleus and hence, do not participate in bonding. This is called inert pair effect.
- SO₃ acts as an electrophile because the highly electronegative oxygen atoms are attached to sulphur atom therefore, S becomes electron deficient and acquires a positive charge due to resonance. Hence, SO₃ acts as an electrophile.

7. (i) Al reacts with conc. HNO₃ to form a protective layer of aluminium oxide on its surface which prevents it from further reaction.

$$2Al_{(s)} + 6HNO_{3(conc.)} \longrightarrow Al_2O_{3(s)} + 6NO_{2(g)}$$
Alumina

(a passive protective layer)

$$+ 3H_2O_{(l)}$$

Therefore, Al becomes passive and thus, aluminium containers can be used to store conc. HNO₃.

(ii) NaOH reacts with Al to evolve dihydrogen gas. The pressure of the hydrogen gas can be used to open drains.

$$2Al + 2NaOH + 6H2O \longrightarrow 2Na[Al(OH)4] + 3H2$$

8.
$$CH_2 = CH = CH = CH = CH - OCH - OCH = CH - OCH =$$

Structure (I) is most stable since both C and O atoms has an octet of electrons and none of these atoms carries any charge. Structures (II and III) both involve separation of charge and hence both are less stable than structure (I). However, structure (II) is more stable than structure (III) since it carries a –ve charge on the more electronegative O atom and +ve charge on the less electronegative C atom which is reverse in structure III. Thus, the decreasing order of stability is : I > II > III.

OR

Wt. of organic compound = 0.2475 gWt. of CO₂ produced = 0.4950 gWt. of H₂O produced = 0.2025 g

Percentage of carbon:

$$= \frac{12}{44} \times \frac{\text{Wt. of CO}_2 \text{ formed}}{\text{Wt. of compound taken}} \times 100$$
$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

Percentage of hydrogen:

$$= \frac{2}{18} \times \frac{\text{Wt. of H}_2\text{O formed}}{\text{Wt. of compound taken}} \times 100$$
$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

9. Since, compound 'A' of boron reacts with NMe₃ to give an adduct 'B'. Thus, compound 'A' is a Lewis acid. Since, adduct 'B' on hydrolysis gives an acid 'C' and hydrogen gas, therefore, 'A' is B₂H₆ and 'C' is boric acid.

$$B_2H_6 + 2NMe_3 \longrightarrow 2BH_3 \cdot NMe_3$$
Diborane Adduct
'A' 'B'

 $BH_3 \cdot NMe_3 + 3H_2O \longrightarrow H_3BO_3$
Boric acid
'C'

10. Volume of nitrogen collected at 300 K and 715 mm pressure = 50 mL

Actual pressure of the gas =
$$715 - 15 = 700 \text{ mm}$$

Volume of nitrogen at STP = $\frac{273 \times 700 \times 50}{300 \times 760}$
= 41.9 mL

22400 mL of N_2 at STP weighs = 28 g

$$\therefore$$
 41.9 mL of nitrogen weighs = $\frac{28 \times 41.9}{22400}$ g

$$\therefore \text{ Percentage of nitrogen} = \frac{28 \times 41.9 \times 100}{22400 \times 0.3}$$
$$= 17.46\%$$

11. (i) On heating borax first loses water molecules and swells up. On further heating it turns to transparent liquid which solidifies into glass like material called borax bead.

$$\begin{array}{ccc} \text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O} \xrightarrow{\text{Heat}} & \text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\text{Heat}} \\ & & & & \text{2NaBO}_2 + \text{B}_2\text{O}_3 \\ & & & & \text{Sodium} & \text{Boric} \\ & & & & \text{metaborate} & \text{anhydride} \\ & & & & & & \\ & & & & & & \\ \end{array}$$

- (ii) Boric acid acts as Lewis acid
 B(OH)₃ + H₂O → [B(OH)₄]⁻ + H₃O⁺
- (iii) Liberates hydrogen $2Al + 6HCl \rightarrow 2Al^{3+} + 6Cl^{-} + 3H_{2}$
- **12.** (i) (a) C—Br because Br is more electronegative than H.
 - (b) C—O because O is more electronegative than nitrogen.
 - (ii) Preparation of CO and CO_2 in Laboratory :

HCOOH
$$\xrightarrow{\text{H}_2\text{SO}_4}$$
 $\xrightarrow{373-473 \text{ K}}$ CO + H₂O;
Formic acid CaCO₃ + 2HCl \longrightarrow CaCl₂ + CO₂ + H₂O Commercial preparation of CO and CO₂:

$$C_{(s)} + H_2O_{(g)} \xrightarrow{473 - 1273 \text{ K}} \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$$

$$\begin{array}{cccc} C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH & + & 2CO_2 \\ & & & & & & \\ Glucose & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\$$

 Lead slowly dissolves in water containing dissolved air forming lead hydroxide which makes water poisonous.

$$2Pb + O_2 + 2H_2O \longrightarrow 2Pb(OH)_2$$

This dissolution of lead in water is called plumbosolvency. It increases if water contains nitrates, organic acids and ammonium salts. However, presence of salts like phosphates, carbonates and sulphates in water retards plumbo-solvency since they form a coating of the corresponding insoluble lead salts on the surface of the lead pipe which protects it from further action. Since hard water

contains chlorides, sulphates and carbonates of Ca²⁺ or Mg²⁺ which form the corresponding insoluble lead salts, therefore, hard water has no action on lead pipes.

14. Mass of $Mg_2P_2O_7$ formed = 0.22 g Now, 1 mole of $Mg_2P_2O_7 \equiv 2$ g atoms of P or $(2 \times 24 + 2 \times 31 + 16 \times 7) = 222$ g of $Mg_2P_2O_7 \equiv 62$ g of P

i.e., 222 g of $Mg_2P_2O_7$ contains phosphorus = 62 g ∴ 0.22 g of $Mg_2P_2O_7$ will contain phosphorus

$$=\frac{62}{222}\times0.22 \text{ g}$$

But this is the amount of phosphorus present in 0.12 g of the organic compound.

$$\therefore \text{ Percentage of phosphorus} = \frac{62}{222} \times \frac{0.22}{0.12} \times 100$$
$$= 51.20$$

- 5. (i) In gallium, the poor shielding of valence electrons by the intervening 3*d*-electrons, the valence electrons remain fairly tightly held by the nucleus. Therefore, effective nuclear charge acting on Ga is slightly higher than that on Al, which results in decrease in atomic radius. Hence, the ionisation enthalpy of gallium is higher than that of aluminium.
 - (ii) Due to small size of boron, the sum of its first three ionisation enthalpies is very high. This prevents it to form +3 ion and forces only the formation of covalent compounds. Therefore, boron does not exist as B³⁺ ion.
 - (iii) Aluminium forms [AIF₆]³⁻ ion because of the presence of vacant *d*-orbitals so, it can expand its coordination number from 4 to 6.
 On the other hand, boron does not form [BF₆]³⁻ ion due to absence of *d*-orbitals.

16. Inductive Effect Resonance Effect

It involves displacement of only σ -electrons and hence, occurs only in saturated compounds. It involves delocalisation of π or n (lone pairs) of electrons and hence, occurs in unsaturated and conjugated

and hence, occurs in unsaturated and conjugated systems.

During inductive effect, the electron pair is only slightly displaced towards the more electronegative atom and hence, only partial positive and negative charges appear.

During resonance effect, the electron pair is completely transferred and hence, full positive and negative charges appear.

Inductive effects are transmitted over short distance in saturated carbon chains and the magnitude of the effect decreases rapidly as the distance from the substituent (electron-withdrawing or electron-donating group) increases. The effect almost becomes negligible beyond three carbon atoms.

The resonance effects are transmitted all along the length of the conjugated system without suffering much change in magnitude. *e.g.*, C_3 , in crotonaldehyde is almost as positive as C_1 .

$$CH_{3}-CH=CH-CH=O \longleftrightarrow CH_{3}-CH=CH-CH=O^{-} \longleftrightarrow CH_{3}-CH=CH-CH=O^{-} \longleftrightarrow CH_{3}-CH=CH=CH-O^{-} \longleftrightarrow CH_{3}-CH=CH-O^{-} \longleftrightarrow$$

17. (i) Na₂B₄O₇ + 2HCl + 5H₂O
$$\Longrightarrow$$
 2NaCl + 4H₃BO₃
Borax Orthoboric acid

A 270 K

(ii)
$$H_3BO_3 \xrightarrow{\Delta, 370 \text{ K}} HBO_2 + H_2O$$

$$\xrightarrow{X} Metaboric acid$$
 $4HBO_2 \xrightarrow{\Delta > 370 \text{ K}} [H_2B_4O_7] \xrightarrow{Red} 2B_2O_3 + H_2O$

$$\xrightarrow{Tetraboric acid} Boron oxide$$
 Z

hybridisation state of B is sp^3 .

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$$

$$B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$$

AlCl₃ in acidified aqueous solution forms octahedral $[Al(H_2O)_6]^{3+}$ ion. In this complex, the 3d orbitals of Al are involved and the hybridisation state of Al is sp^3d^2 .

$$AlCl_3 + H_2O \xrightarrow{HCl} [Al(H_2O)_6]^{3+} + 3Cl_{(aq)}^{-}$$

Electronic configuration of Al³⁺

OR

In trivalent state, most of the compounds being covalent are hydrolysed by water, e.g., BCl₃ on hydrolysis in water forms [B(OH)₄]⁻ species, the

Formation of
$$[Al(H_2O)_6]^{3+}$$
 sp^3d^2 hybridisation

18. 2-methylbutane has four different sets of equivalent H-atoms.

Removal of H– atom from any of these equivalent sets gives four different carbocations as shown:

sets gives four different carbocations as shown:

$$CH_3 \xrightarrow{\beta} CH \xrightarrow{c} CH_2 \xrightarrow{c} CH_2$$

$$CH_3 \xrightarrow{c} CH_3$$

$$(I)(1^\circ)$$

$$CH_3 \xrightarrow{c} CH_2 \xrightarrow{c} CH_3$$

$$CH_3 \xrightarrow{c} CH_2 \xrightarrow{c} CH_2 \xrightarrow{c} CH_2 \xrightarrow{c} CH_3$$

$$CH_3 \xrightarrow{c} CH_3$$

$$CH_3$$

Stability of carbocation decreases in the order $3^{\circ} > 2^{\circ} > 1^{\circ}$. So, III (3° carbocation) is most stable followed by II (2° carbocation). Out of I and IV (both are 1° carbocations) I has a CH₃ group at β -carbon while IV has a CH₃ group at α -carbon. As +I – effect decreases with distance, hence IV is more stable than I. Therefore, the overall stability of these four carbocations increases in the order :

- **19.** (i) Sublimation: Camphor sublimes while common salt remains as residue in the China dish.
 - (ii) Since the two liquids are immiscible, the technique of solvent extraction with a separating funnel is used. The mixture is thoroughly shaken and the separating funnel is allowed to stand. Kerosene being lighter than water forms the upper layer while water forms the lower layer.

The lower water layer is run off when kerosene oil is obtained. It is dried over anhydrous CaCl₂ or MgSO₄ and distilled to give pure kerosene oil.

- (iii) Distillation under reduced pressure.
- **20.** (i) CO being a good reducing agent, reduces several metal oxides (except alkali and alkaline earth metal oxides) into crude metal. Thus, it is used in the extraction of metals.
 - (ii) CO forms carboxyhaemoglobin complex with haemoglobin (the red pigment which carries oxygen) of blood which is about 300 times more

- stable than oxygen-haemoglobin complex and thus, it stops the supply of oxygen and hence, leads to death of the person.
- (iii) Solid CO₂, produces cooling and sublimes directly into vapour state. Thus, it is used for refrigeration.
- **21.** Both carbocations (i) and (ii) are stabilised by hyperconjugation as shown below:

(i)
$$H - \overset{H}{\overset{\vdash}{C}} \overset{+}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow H - \overset{H^+}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow H - \overset{H}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow H - \overset{H}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow etc.$$
 $H \overset{H}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow H - \overset{H}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow etc.$
 $H \overset{H}{\overset{\vdash}{C}} \overset{CH_3}{\overset{\vdash}{C}} \longleftrightarrow D - \overset{C}{\overset{\vdash}{C}} \overset{CD_3}{\overset{\vdash}{C}} \longleftrightarrow etc.$
 $U \overset{D}{\overset{\vdash}{C}} \overset{CD_3}{\overset{\vdash}{C}} \longleftrightarrow D - \overset{C}{\overset{\vdash}{C}} \overset{CD_3}{\overset{\vdash}{C}} \longleftrightarrow etc.$
 $U \overset{D}{\overset{\vdash}{C}} \overset{CD_3}{\overset{\vdash}{C}} \longleftrightarrow D - \overset{C}{\overset{\vdash}{C}} \overset{CD_3}{\overset{\vdash}{C}} \longleftrightarrow etc.$

Due to stronger C—D bond, contribution of structures (V-VIII) towards stability of carbocation, $(CD_3)_3C^+$ is less than those of structures (I-IV) for carbocation, $(CH_3)_3C^+$, therefore, carbocation (i) is more stable than carbocation (ii).

22. When borax is heated on a platinum wire loop, a transparent glassy bead called the borax bead is formed.

$$\begin{array}{c} \text{Na}_2 \text{B}_4 \text{O}_7 \cdot 10 \text{H}_2 \text{O} \xrightarrow{\text{Heat} \atop -10 \text{H}_2 \text{O}} \Rightarrow \text{Na}_2 \text{B}_4 \text{O}_7 \xrightarrow{\text{Red hot}} \Rightarrow \\ & 2 \text{Na} \text{BO}_2 + \text{B}_2 \text{O}_3 \\ & \underbrace{\text{Sod. metaborate} \quad \text{Boric anhydride}}_{\text{Transparent glassy bead}} \end{array}$$

When this transparent glassy bead is heated with CuO in the oxidising flame, it imparts blue colour to the bead due to the formation of cupric metaborate.

$$\begin{array}{c} \text{CuO} + \text{B}_2\text{O}_3 \xrightarrow{\text{Oxidising flame}} & \text{Cu(BO}_2)_2 \\ \text{Cupric oxide} & \text{Cupric metaborate} \\ & \text{(blue)} \end{array}$$

However, when cupric metaborate is heated in the reducing flame of the bunsen burner, the blue cupric metaborate is reduced by carbon present in the flame first to colourless cuprous metaborate and then to metal.

- 23. (i) Ethyl alcohol, C₂H₅OH
 - (ii) Ethanol, CH₃CH₂OH
 - (iii) Alcohol acts as depressant on the central nervous system. It has a complex mode of action and affects multiple systems in the brain. Its long term consumption may cause irreversible damage to the liver.
 - (iv) Values possessed by Rahul are love, care and worry for his father.
- 24. (i) When an aqueous solution of borax is acidified with HCl, boric acid is formed.

 $Na_2B_4O_7 + 2HCl + 5H_2O \longrightarrow 2NaCl + 4H_3BO_3$ Boric acid is a white crystalline solid. It is soapy to touch because of its planar layered structure. Boric acid is a weak monobasic acid. It is not a protonic acid but acts as a Lewis acid

by accepting electrons from a hydroxyl ion. $B(OH)_3 + 2H_2O \longrightarrow [B(OH)_4]^- + H_3O^+$

(ii) (a) Anhydrous HF is a covalent compound and is strongly hydrogen-bonded. Therefore, it does not give F⁻ ions and hence AlF₃ does not dissolve in HF. Whereas, NaF is an ionic compound. It contains F ions which combine with electron deficient AlF₃ to form the soluble complex.

$$3NaF + AlF_3 \longrightarrow Na_3[AlF_6]$$
Sodium hexafluoroaluminate (III)
(Soluble complex)

(b) Boron due to its small size and higher electronegativity has greater tendency to form complexes than aluminium. Hence, precipitation of AlF₃ takes place when BF₃ is passed through Na₃[AlF₆].

$$Na_3[AlF_6] + 3BF_3 \longrightarrow 3Na^+[BF_4]^- + AlF_3$$

Sodium
tetrafluoroborate (III)
(soluble complex)

(i)
$$4BF_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3LiF + 3AlF_3$$
 Z
Diborane
 X
 $B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$
 X
Orthoboric acid
 Y
 $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

(ii) (a) Carbon because of its small size and higher electronegativity than silicon forms $p\pi - p\pi$ double bonds with O-atoms to form CO₂ molecule. These molecules of CO₂ are held together by weak van der Waals forces of attraction which can be easily overcome by collisions of the molecules at room temperature. Consequently, CO₂ is a gas. Silicon, on the other hand, because of its bigger size and lower electronegativity than carbon has little tendency to form $p\pi$ – $p\pi$ double bonds with O-atoms. Instead, each silicon atom forms four single covalent bonds with O-atoms which are tetrahedrally arranged around it leading to the formation of a threedimensional network structure. To break these covalent bonds, a large amount of energy is needed and hence, SiO₂ is a high melting solid.

- (b) SiF₆²⁻ is known whereas corresponding fluoro compound of carbon is not known as Si atom has vacant 3d-orbitals available to accommodate electrons and expand its coordination number upto 6 whereas carbon atom does not have 3*d*-orbitals.
- **25.** (a) Vol. of M/10 H_2SO_4 taken = 100 mL Let us first calculate the volume of excess M/10 H₂SO₄ which was neutralised by 154 mL of M/10 NaOH

154 mL of
$$\frac{M}{10}$$
 NaOH $\equiv \frac{154}{2}$ mL of $\frac{M}{10}$ H₂SO₄

 \therefore Volume of $\frac{M}{10}$ H₂SO₄ left unused = 77 mL

Volume of $\frac{M}{10}$ H₂SO₄ used for neutralisation of NH₃ = 100 – 77 = 23 mL

Now,

23 mL of
$$\frac{M}{10}$$
 H₂SO₄ $\equiv 2 \times 23$ mL of $\frac{M}{10}$ NH₃ $\equiv 46$ mL of $\frac{M}{10}$ NH₃

Now, 1000 mL of 1 M NH₃ contain nitrogen = 14 g 46 mL of $\frac{M}{10}$ NH₃ contain nitrogen

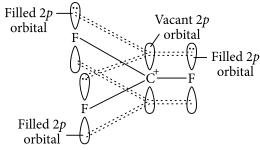
$$=\frac{14}{1000}\times\frac{46\times1}{10}$$

Percentage of nitrogen = $\frac{14 \times 46 \times 100}{1000 \times 10 \times 0.35}$ = 18.4%

(b) In F_3C — $\overset{+}{C}$, the strongly withdrawing F_3C —group withdraws electrons of the C—C bond towards itself. As a result, the positive charge on C gets intensified and therefore, F_3C — $\overset{+}{C}$ is less stable. On the other hand, in carbocation $F_3\overset{+}{C}$ lone pair of electrons on each of the three F-atoms overlaps with the empty 2p-orbital of the carbon atom carrying the +ve charge thereby dispersing the positive charge and thus stabilizing the carbocation $F_3\overset{+}{C}$ relative to F_3C — $\overset{+}{C}$



-I-effect of the F atoms destabilises the carbocation by intensifying the +ve charge.



Back bonding from 2*p* orbitals of F to empty 2*p* orbital of C disperses +ve charge.

OR

(a) Percentage of carbon = 69% Amount of carbon in 0.20 g of compound

$$=0.2 \times \frac{69}{100} = 0.138 \text{ g}$$

Percentage of hydrogen = 4.8 %

Amount of hydrogen in 0.20 g of compound

$$=\frac{0.2\times4.8}{100}=0.0096$$
 g

Now, $C \equiv CO_2$

12 g of carbon on combustion gives $CO_2 = 44$ g 0.138 g of carbon on combustion will give CO_2

$$=\frac{44}{12}\times0.138=0.506$$
 g

 $2H \equiv H_2O$

2 g of hydrogen on combustion gives water = 18 g 0.0096 g of hydrogen on combustion will give

water =
$$\frac{18}{2} \times 0.0096 = 0.0864$$
 g

- **(b)** Benzoic acid can be purified from hot water because of the following characteristics:
 - (i) Benzoic acid is more soluble in hot water but less soluble in cold water.
 - (ii) Impurities present in benzoic acid are either insoluble in water or are more soluble in water to such an extent that when a hot saturated solution of benzoic acid is cooled, the impurities remain in the solution. Since impure benzoic acid satisfies both these conditions, it can be purified by crystallisation.
- 26. (i) (a) When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573 K various types of methyl substituted chlorosilanes of formula MeSiCl₃, Me₂SiCl₂, Me₃SiCl with small amount of Me₄Si are formed.

$$2\text{CH}_3\text{Cl} + \text{Si} \xrightarrow{\text{Cu powder}} \text{CH}_3\text{)SiCl}_3 \\ + (\text{CH}_3)_2\text{SiCl}_2 + (\text{CH}_3)_3\text{SiCl} + (\text{CH}_3)_4\text{Si}$$

(b) When silicon dioxide is treated with HF, silicon tetrafluoride is formed.

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

(c) CO is a powerful reducing agent, it reduces ZnO to Zn.

$$CO_{(g)} + ZnO_{(s)} \xrightarrow{\Delta} Zn_{(s)} + CO_{2(g)} \uparrow$$

(ii) Since metal 'X' reacts with NaOH to first give a white ppt. 'A' which dissolves in

excess of NaOH to give a soluble complex 'B', therefore, metal 'X' must be Al; ppt A must be Al(OH)3 and complex 'B' must be sodiumtetrahydroxoaluminate (III)

$$2Al + 3NaOH \longrightarrow Al(OH)_3 \downarrow + 3Na^+$$
'X' Aluminium hydroxide
$$Al(OH)_3 + NaOH \longrightarrow Na^+[Al(OH)_4]^-$$
'A' 'B'

Sod. tetrahydroxoaluminate (III)

Since 'A', i.e., Al(OH)₃ reacts with dil. HCl to give compound 'C', therefore, 'C' must be AlCl₃. $Al(OH)_3 + 3HCl \longrightarrow AlCl_3 + 3H_2O$

Since 'A' on heating gives 'D' which is used to extract metal (i.e., electrolysis of Al₂O₃ gives Al metal), therefore, 'D' must be alumina (Al₂O₃) $2\text{Al(OH)}_3 \xrightarrow{\Delta} \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$

- (i) (a) Due to inert pair effect, Pb is more stable in +2 state than in +4 oxidation state. Therefore, lead (II) chloride does not react with Cl₂ to give lead (IV) chloride.
 - (b) Lead (IV) chloride on heating decomposes to give lead (II) chloride and Cl₂ because lead in +2 oxidation state is more stable than in +4 oxidation state.

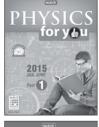
$$PbCl_{4(l)} \longrightarrow PbCl_{2(s)} + Cl_{2(g)}$$

- (c) Due to strong oxidising power of Pb⁴⁺ ion and reducing power of I ion, PbI4 does
- (ii) (a) CCl₄ cannot be hydrolysed by water because carbon atom cannot accommodate lone pair of electrons from oxygen atom of water due to absence of *d*-orbitals. While, SiCl₄ can be hydrolysed to give Si(OH)₄ due to presence of *d*-orbitals.

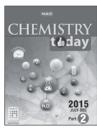
(b) Carbon has a strong tendency for catenation compared to silicon due to smaller size and higher electronegativity of carbon atom and unique strength of C-C bonds.

The bond dissociation energy decreases as the atomic size increases. Down the group atomic size increases. Since, the atomic size of carbon is much smaller than silicon therefore, carbon-carbon bond dissociation energy is higher than that of silicon-silicon bond dissociation energy. Due to this, carbon has a strong tendency for catenation as compared to silicon.

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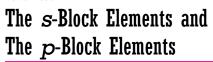
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MPP-6 MONTHLY Practice Problems

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.



Total Marks: 120 Time Taken: 60 Min.

NEET / AIIMS

Only One Option Correct Type

- **1.** Which of the following compounds is converted into the dimer form?
 - (a) BF₃
- (b) BH₃
- (c) BCl₃
- (d) BBr₃
- **2.** Which of the following carbonates decomposes most easily on heating?
 - (a) Rb₂CO₃
- (b) K_2CO_3
- (c) Na₂CO₃
- (d) MgCO₃
- **3.** When orthoboric acid (H₃BO₃) is strongly heated, the residue left is
 - (a) metaboric acid
- (b) boron
- (c) boric anhydride
- (d) borax.
- 4. Iron pipes lying under acidic soil are often attached to blocks of magnesium for protection from rusting. Magnesium offers protection to iron against corrosion because it
 - (a) is more readily converted into positive ions
 - (b) is more stable than ion
 - (c) forms a corrosion resistance alloy with iron
 - (d) prevents air from reaching the surface of iron.
- **5.** KO₂(potassium superoxide) is used in oxygen cylinders in space and submarines because it
 - (a) absorbs CO₂ and increases O₂ contents
 - (b) eliminates moisture
 - (c) absorbs CO₂
 - (d) produces ozone.

- **6.** Solid CO₂ is known as dry ice, because
 - (a) it evaporates at 40°C
 - (b) it melts at 0°C
 - (c) its boiling point is more than 199°C
 - (d) it evaporates at -78.5°C without melting.

Class X

7. In the replacement reaction,

$$\geq$$
CI + MF \longrightarrow \geq CF + MI

The reaction will be most favourable if M happens to be

- (a) Na
- (b) K
- (c) Rb
- (d) Li.

8.
$$PbO_2 \longrightarrow PbO \quad \Delta G_{298} < 0$$

$$SnO_2 \longrightarrow SnO \quad \Delta G_{298} > 0$$

Most probable oxidation state of Pb and Sn will be

- (a) Pb⁴⁺, Sn⁴⁺
- (b) Pb^{4+} , Sn^{2+}
- (c) Pb^{2+} , Sn^{2+}
- (d) Pb^{2+} , Sn^{4+}
- **9.** In curing cement plasters, water is sprinkled from time to time. This helps in
 - (a) developing interlocking needle like crystals of hydrated silicates
 - (b) hydrated sand gravel mixed with cement
 - (c) converting sand into silicic acid
 - (d) keeping it cool.
- 10. Alum helps in purifying water by
 - (a) forming Si complex with clay particles
 - (b) sulphate part which combines with the dirt and removes it
 - (c) aluminium which coagulates the mud particles
 - (d) making mud water soluble.

- **11.** The solubility of calcium acetate decreases while that of lead nitrate increases with increase in temperature. This is because
 - (a) calcium acetate shows exothermic dissolution whereas Pb(NO₃)₂ shows endothermic dissolution.
 - (b) calcium acetate decomposes to CaCO₃ which is water insoluble.
 - (c) hydration energy of calcium acetate is lower than that of Pb(NO₃)₂.
 - (d) nitrates are more soluble than acetates of metals.
- 12. Percentage of lead in lead pencil is
 - (a) 30

(b) 20

(c) 10

(d) zero.

Assertion & Reason Type

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- **13. Assertion:** Magnesium is extracted by the electrolysis of fused mixture of MgCl₂, NaCl and CaCl₂.

Reason: Calcium chloride acts as a reducing agent.

14. Assertion : $Al(OH)_3$ is insoluble in NH_4OH but soluble in NaOH.

Reason: NaOH is strong alkali.

15. Assertion : Potassium and caesium emit electrons on exposure to light.

Reason : Potassium and caesium are used in photo electric cells.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

- **16.** The atomic radii of alkali metals M lie in the order Li < Na < K < Rb but the radii of M^+ ions in aqueous solution lie in the reverse order Li⁺ > Na⁺ > K⁺ > Rb⁺. What is the reason for this reverse order (on going from Li to Rb)?
 - (a) Gradual increase in ionisation energy
 - (b) Increasing weakness of the metallic bond
 - (c) Increasing electropositive character
 - (d) Decreasing degree of hydration

- 17. Among the halides,
 - (i) BCl₃

(ii) AlCl₃

(iii) GaCl₃

(iv) InCl₃

the order of decreasing Lewis acid character is

- (a) (i), (ii), (iii), (iv)
- (b) (iv), (iii), (ii), (i)
- (c) (iii), (iv), (ii), (i)
- (d) (ii), (iii), (iv), (i)
- **18.** A white solid *X* is a compound of *s*-block element. A piece of red litmus paper turns white when it is dipped into a freshly made aqueous solution of the the white solid. The white solid 'X' is
 - (a) Na_2O_2
 - (b) Na₂O
 - (c) CaO
 - (d) both Na₂O₂ and Na₂O
- 19. Select the incorrect statement.
 - (a) In $Si_2O_7^{6-}$, there is one shared oxygen.
 - (b) $Si_6O_{18}^{12}$ represents a cyclic silicate with two shared oxygen per silicon atom.
 - (c) Pyroxene is a linear chain silicate with two shared oxygen per silicon atom.
 - (d) In three dimensional network silicate, there are three shared oxygen per silicon atom.

More than One Options Correct Type

- **20.** Highly pure dilute solution of sodium in liquid ammonia
 - (a) shows blue colour
 - (b) exhibits electric conductivity
 - (c) produces sodium amide
 - (d) produces hydrogen gas.
- **21.** Select the correct statement(s).
 - (a) BF₃ fumes strongly in moist air and is partially hydrolysed by excess of water.
 - (b) BF $_3$ is converted into the adducts BF $_3$ · H $_2$ O and BF $_3$ · 2H $_2$ O with small amounts of water at low temperature.
 - (c) H₃BO₃ is a weak acid but HBF₄ is a very strong acid.
 - (d) KBF₄ is sparingly soluble is water.

- 22. Which of the following groups of elements have chemical properties that are most similar?
 - (a) Be, Al, Ca
 - (b) Mg, Ba, Sr
 - (c) Be, Ra, Cs
 - (d) Na, K, Ca
- 23. The composition of white lead is
 - (a) $2PbCO_3 \cdot Pb(OH)_2$
 - (b) $Pb(HCO_3)_2$
 - (c) $Pb(OH)_2 \cdot 2PbCO_3$
 - (d) $Pb(OH)_2 \cdot PbCO_3$

Integer Answer Type

- **24.** Number of B O B bonds in borax is
- 25. One mole of lithium nitride is decomposed by H₂O and resultant solution is neutralised by HCl. Number of moles of HCl required is
- 26. Amongst the following, the maximum number of compounds showing basic nature is B₂O₃, B(OH)₃, Al₂O₃, Al(OH)₃, Ga₂O₃, Ga(OH)₃, Tl₂O₃, Tl₂O, Ti(OH)₃, TlOH

Comprehension Type

'A' burns in nitrogen and forms 'B' (Ionic Compound)

$$^{`B'} + H_2O \longrightarrow ^{`C'} + ^{`D'}$$
(Ionic compound)

 $C'_{(aq)} + CO_2 \longrightarrow Milkiness appears$

Consider the above information and answer the following questions.

- **27.** The element 'A' is
 - (a) alkali metal
 - (b) alkaline earth metal
 - (c) magnesium
 - (d) barium.

- 28. The milkiness that appears is due to
 - (a) $Ca(OH)_2$
 - (b) $Ca(HCO_3)_2$
 - (c) $Ba(HCO_3)_2$

Column I

Column I

(d) BaCO₃

Matrix Match Type

29. Match the entries listed in column I with appropriate entries listed in column II.

Column II

Column II

	Column	L		Column 11			
(A)	Silicates		(P)	P) Chemically inert			
(B)	Silicones		(Q)	Exists in planar form			
(C)	Trimethy	amine	(R)	Nitrogen is sp ³	3		
(D) Trisilyl amine			(S)	hybridised S) Contains Si—O—Si bonds			
	A	В	C	D			
(a)	P, Q	P, Q, S	R	Q			
(b)	R, S	P, Q	P	S			
(c)	Q, S	R, P	S, I	R Q			
(d)	S, Q	P, Q, R	S, I	R P, R			

30. Match the entries listed in column I with appropriate entries listed in column II.

Coluilli	11	C	Column 11			
(A) BeO		(P) Di	(P) Diagonal relationship			
(B) Al_2O_3		(Q) Ba	(Q) Baryta water			
(C) MgO		(R) W	ater ins	oluble		
(D) CaO		(S) Es	timatio	n by EDTA		
A	В	C	D			
(a) Q, S	P, R	S	Q			
(b) P, Q	Q, R	R, S	P			
(c) P, Q, R	S, P	P	R			
(d) P, R	P, R	P, S	S	♦		

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No. of questions attempted No. of questions correct

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You need to score more next time.

< 60%

NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.



Class



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ALDEHYDES AND KETONES

CARBOXYLIC ACIDS

ALDEHYDES AND KETONES

Introduction

- These are the compounds with carbon-oxygen double bond (>C=O) called carbonyl group having general formula $C_nH_{2n}O$.
- Aldehydes contain carbonyl group attached to either two H-atoms or one H-atom and one C-atom of an alkyl/aryl group.

O (where
$$R = H$$
 or $R = H$ or any alkyl, aralkyl or aryl group)

Aldehydes

O (R)

R C R

Ketone

If the two R and R' groups are different, the ketone is called a mixed ketone and if R and R' represent the same group, the ketone is referred to as simple ketone.

$$CH_3$$
 $C=0$
 CH_3
 $C=0$
 CH_3
 $C=0$
 CH_3
 $C=0$
 CH_3
 $C=0$
 CH_3
 $C=0$
 CH_3

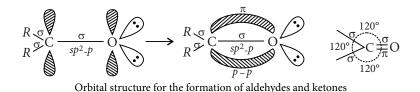
The functional group of aldehydes is called the aldehydic group $\begin{pmatrix} O \\ || \\ -C-H \end{pmatrix}$ while that of the ketones is called the ketonic group (>C=O).

Nomenclature

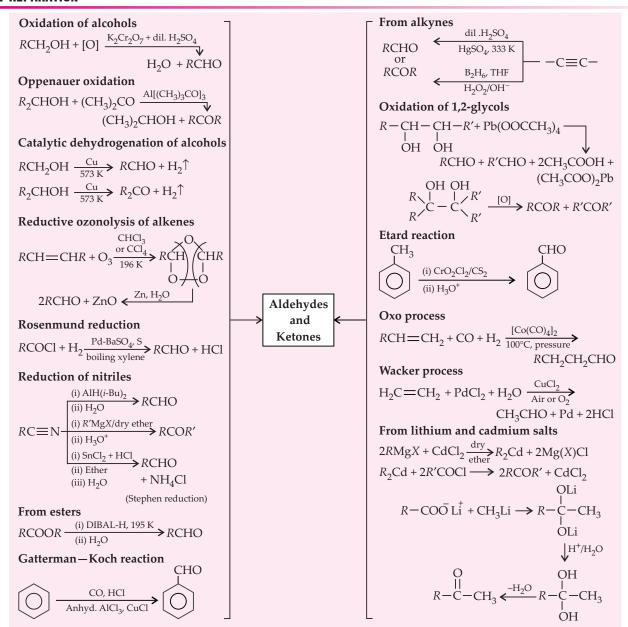
- The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending -'ic' of acid with aldehyde.
 - The location of the substituent in the carbon chain is indicated by Greek letters α , β , γ , δ , etc
 - The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group.
 - > The locations of substituents are indicated by Greek letters, α α' , β β' and so on beginning with the carbon atoms next to the carbonyl group, indicated as α α' .
 - The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending -'e' with -'al' and -'one' respectively.

Compound	Common name	IUPAC name
CH ₃ CH(OCH ₃)CHO	lpha-Methoxypropionaldehyde	2-Methoxypropanal
CH ₃ COC ₂ H ₅	Ethylmethylketone	Butan-2-one

STRUCTURE



PREPARATION



Chemical properties

Physical state and odour: Lower members of aldehydes and ketones (upto C_{10}) are colourless volatile liquids except formaldehyde which is gas at ordinary temperature.

- Higher members of aldehydes and ketones are solids with fruity odour.
- Lower aldehydes have unpleasant odour but ketones possess pleasant smell.

Solubility: Lower members of aldehydes and ketones (upto C₄) are soluble in water due to H-bonding between polar carbonyl group and water.

- However, solubility decreases with increase in molecular weight.
- Aromatic aldehydes and ketones are much less soluble than corresponding aliphatic aldehydes and ketones due to larger benzene ring.
- However, all carbonyl compounds are fairly soluble in organic solvents.

Boiling points: Slightly lower than corresponding alcohol due to lack of hydrogen bonding.

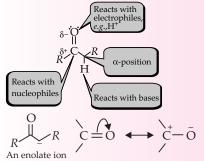
Their boiling points are slightly higher than those of corresponding non-polar hydrocarbons or weakly polar ethers. This is due to intermolecular association due to dipole-dipole interaction among polar aldehydes or ketones.

Intermolecular dipole-dipole attraction

Among isomeric aldehydes and ketones, boiling points of ketones are slightly higher than those of aldehydes due to the presence of two electron donating alkyl groups making them more polar.

Polar nature of carbonyl group

- All aldehydes (RCHO) and ketones (RCOR) contain a polar C=O bond.
- The more electronegative oxygen atom attracts the electron towards itself. The oxygen atom reacts with electrophiles and the carbon atom reacts with nucleophiles.



Acidity of α -Hs: The α -hydrogens of aldehydes and ketones are weakly acidic due to

- *I*-effect of the C=O group, reduces the electron density in the C_α-H bond.
- the carbanion or the enolate ion left after the removal of the proton is stabilised by resonance.

HO⁻ + -C-C-H
$$\rightarrow$$

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Relative reactivities of aldehydes and ketones:

Due to inductive effect:

$$\begin{array}{c}
H \\
C = O \\
\end{array}$$
 $\begin{array}{c}
R \\
C = O
\end{array}$
 $\begin{array}{c}
R \\
R$
 $\begin{array}{c}
C = O
\end{array}$

Formaldehyde Any other aldehyde Ketone (no alkyl group) (one alkyl group) (two alkyl groups)

Due to steric effect:

H C = O >
$$\frac{\text{CH}_3}{\text{H}}$$
 C = O > $\frac{\text{CH}_3}{\text{CH}_3}$ C = O

Formaldehyde Acetaldehyle Acetone

> $\frac{(\text{CH}_3)_2\text{CH}}{(\text{CH}_3)_2\text{CH}}$ C = O > $\frac{(\text{CH}_3)_3\text{C}}{(\text{CH}_3)_3\text{C}}$ C = O

SOME BASIC CONCEPTS OF CHEMISTRY

Mole concept is the centre of quantitative calculations in chemistry and the multiple interpretations of this concept allow us to bridge the gap between the submicroscopic world of atoms and molecules and the macroscopic world that we can observe.





REACTION KINETICS

Apart from playing an important role in industries and study of biological processes, kinetics also plays a role in environmental and atmospheric chemistry as part of an effort to understand a variety of issues ranging from the fate of prescription pharmaceutical in waste water to cascade of reactions involved in the ozone cycle.

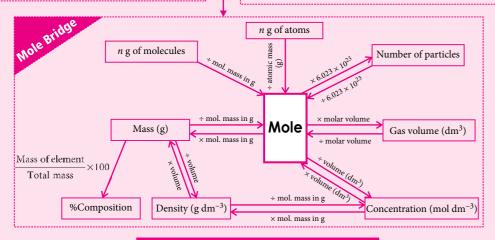


Mole Concept

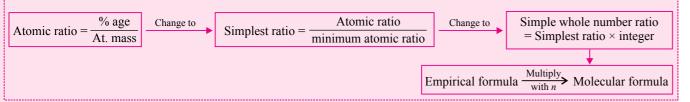
- 1 mole = N_A particles = 6.023×10^{23} particles.
- A mole is defined as the amount of substance that contains the same number of entities (atoms, molecules, ions or other particles), as the number of atoms present in 12 g of the C-12 isotope.
- The number of atoms present in 12 g of C-12 is equal to 6.023×10^{23} .

Have a Look!

- Contrary to belief of chemistry students, 'Avagadros' number was not discovered by Amadeo Avagadro. It is just an honorary name.
- First time number of molecules in any substance was calculated in 1865, by Josef Loschmidt. $(2.6 \times 10^{19} \text{ molecules in one cm}^3 \text{ of a})$ gaseous substance).
- Term Avagadros' number was used by Jean Baptiste Perrin in 1909.
- The unit 'mole' was introduced in 1900 by Ostwald and defined this unit in terms of gram.



Empirical and Molecular Formula



Stoichiometric Calculations

Limiting Reagent

- The limiting reagent or reactant is the reactant that limits the amount of the other reactant that can combine and the amount of product that can form in a chemical reaction.
- The excess reagent is the substance that is not used up completely in a reaction.
- For example, in combustion of 12 g of carbon in excess of oxygen (i.e., more than 32 g of oxygen), carbon acts as the limiting reagent.

Reactions in Solutions

- Mass % = $\frac{W_B \times 100}{}$
- Molarity (M) = $\frac{W_B \times 1000}{M_B \times V \text{ in mL}}$
- Normality (N) = $\frac{W_B \times 1000}{\text{GEM}_B \times V \text{ in mL}}$
- Molality $(m) = \frac{W_B \times 1000}{\text{GMM}_B \times W_A \text{ in g}}$
- Mole fraction, $x_2 = \frac{n_2}{n_1 + n_2}$ and $x_1 = \frac{n_1}{n_1 + n_2}$

Rate of Reaction

Change in concentration of reactants or products as function of time (Unit: $mol L^{-1} s^{-1}$ or $M s^{-1}$)

Differential Rate Equation

Average Rate

$$aA + bB \longrightarrow cC + dD$$

Rate =
$$-\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

Instantaneous Rate



Rate Law/Rate Equation

• The expression of rate in terms of molar concentration of reactants.

For reaction,
$$aA + bB \longrightarrow cC + dD$$

Rate = $k[A]^x[B]^y$

Where,
$$k = \text{rate constant or specific reaction}$$
 rate.

• Depends only upon temperature.

where, n =order of reaction.

• Unit of $k = \left(\frac{\text{mol}}{I}\right)^{1-n} s^{-1}$

Order of Reaction

- Sum of powers of concentration terms in the rate law expression. e.g., Rate = $k[A][B]^2$
- $\therefore \text{ Order} = 1 + 2 = 3$
- For n^{th} order, $t_{1/2} \propto \frac{1}{a^{n-1}}$
- Experimental concept and can be zero or
- Depends upon pressure and temperature.

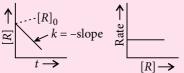
Molecularity of Reaction

- The number of molecules of reactants taking part in elementary step of a reaction.
- Theoretical concept and can never be zero or fractional.
- Independent of pressure and temperature.

Integrated Rate Equation

Zero Order Reaction

- Rate = k or $kt = [R]_0 [R]$
- Unit of $k = \text{mol } L^{-1}s^{-1}$
- $t_{1/2}$ (half-life) = $\frac{[R]_0}{2k}$



First Order Reaction

- Rate = k[R] or $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ Unit of $k = s^{-1}$
- $t_{1/2} = 0.693/k$
- In terms of pressure,

$$k = \frac{1}{t} \log \frac{1}{2p_i - p_t}$$

$$\lim_{K = -\text{slope}} \lim_{k = -\text{slope}} \frac{1}{k}$$

$$\lim_{K = -\text{slope}} \lim_{k = -\text{slope}} \frac{1}{k}$$

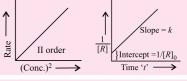
Useful Relations for First Order Reaction

$$t_{75\%} = 2t_{1/2}, t_{87.5\%} = 3t_{1/2}, t_{93.75\%} = 4t_{1/2},$$

 $t_{96.87\%} = 5t_{1/2}, t_{99.9\%} = 10t_{1/2}$

Second Order Reaction

- Rate = $k[R]^2$ or $1/[R]_t = kt + 1/[R]_0$
- Unit of $k = L \text{ mol}^{-1} \text{ s}^{-1}$
- $t_{1/2} = 1/k[R]_0$



nth Order Reaction

- Rate = $k[R]^n$ or $(n-1)kt = \frac{1}{[R]^{n-1}} - \frac{1}{[R]_0^{n-1}}$
- Unit of $k = (\text{mol L}^{-1})^{1-n} s^{-1}$
- $t_{1/2} = 2^{n-1} 1/k(n-1)[R]_0^{n-1}$

Dependency of Rate on Temperature

Arrhenius Equation

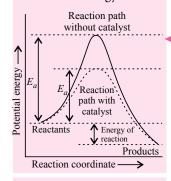
- $k = Ae^{-E_a/RT}$ Here, A = pre-exponential
- factor
- R = Gas constant E_a = Activation energy

Activation Energy (E_{α})

- Energy required by the reactant molecules for effective collisions to form products.
- The slope of $\ln k vs 1/T$ has the value $-E_a/R$ and is used to calculate value of E_a .

Effect of Catalyst on Activation Energy

• A catalyst increases the rate of reaction by providing a path of lower activation energy.

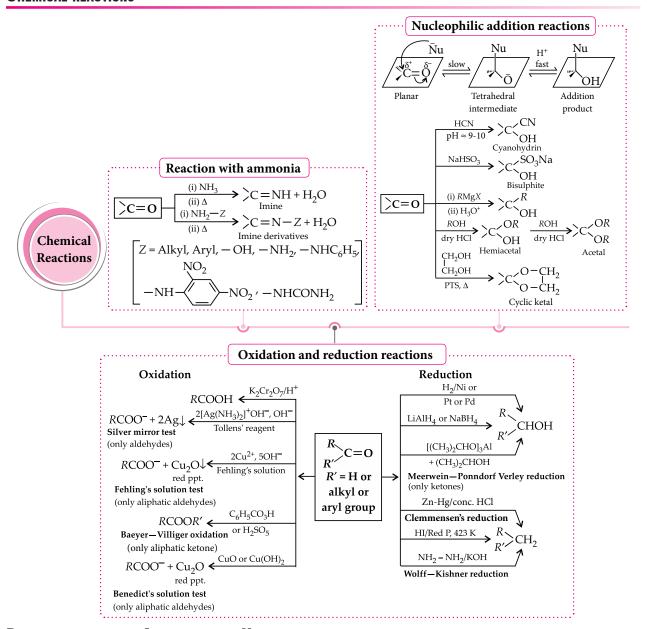


Temperature Coefficient

- It is the ratio of k_{298}
- For every 10° rise in temperature the rate becomes double.

Collision Theory

Rate = $P \cdot Z_{AB} e^{-E_a/RT}$



DISTINCTION BETWEEN ALDEHYDES AND KETONES

Tests with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red precipitate	No precipitate
Tollens' reagent	Black precipitate of silver or silver mirror	No black ppt. or silver mirror
2,4-Dinitrophenylhydrazine	Orange-yellow or red well defined crystals with melting points characteristic of individual aldehydes	Č ,
Alkaline sodium nitroprusside	A deep red colour (only acetaldehyde responds to this test.)	Red colour which changes to orange. (Methyl ketone gives this test)

Some Name Reactions

Haloform reaction: Given by methyl ketones (even acetaldehydes). $2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$ $RCOCH_3 + 3NaOI \longrightarrow RCOONa + CHI_3 + 2NaOH$ Iodoform (yellow ppt.)

Name reactions

Aldol condensation: Aldehyde or ketone containing α-hydrogen on heating with dilute NaOH gives β-hydroxycarbonyl compound

NaOH gives
$$\beta$$
-hydroxycarbonyl compound called aldol.
 $2R - \overset{\circ}{C}H_2 - CH = O$ $\xrightarrow{\text{dil. NaOH}}$ OH R $R - CH_2 - CH - CH - CH = O$ Aldol $A - H_2O$ $A - CH_2 - CH = C - CH = O$ $A - CH_2 - CH = O$ A

Intramolecular aldol condensation takes place in diketones and gives rise to cyclic products. Crossed aldol condensation takes place between two different carbonyl compounds (one of which must have one α -hydrogen).

$$C_{6}H_{5}-C-H+CH_{3}-C-CH_{3} \xrightarrow{\text{(i) dil. NaOH}} C_{6}H_{5}-CH=CH-C-CH_{3}$$

Wittig reaction

$$= O + (C_6H_5)_3P = CH_2 \xrightarrow{\text{THF}} CH_2 + (C_6H_5)_3PC$$

Reaction with ammonia

$$6\text{HCHO} + 4\text{NH}_{3} \xrightarrow[-6\text{H}_{2}\text{O}]{} \text{Hexamethylenetetramine}$$

$$\text{(Urotropine)} \text{(Urotropine)}$$

Tishchenko's reaction

CH₃ - CHO + CH₃ - CHO
$$[CH_3 - COOH + CH_3CH_2OH]$$

$$-H_2O \downarrow \Delta$$

$$CH_3 - C - O - C_2H_5$$

Knoevenagel reaction

$$R > C = O + CH_2 < COOH \xrightarrow{\text{pyridine}/\Delta} R > C = CH - COOH$$

Cannizzaro reaction: Given by aldehydes which have no α -hydrogen atom.

e.g.,
$$2C_6H_5CHO + NaOH \xrightarrow{\Delta} C_6H_5CH_2OH + C_6H_5COONa$$

Crossed Cannizzaro reaction takes place between two different aldehydes and that aldehyde undergoes oxidation which is more reactive towards the nucleophile while the other aldehyde is reduced.

e.g.,
$$C_6H_5CHO + HCHO \xrightarrow{NaOH, \Delta} C_6H_5CH_2OH + HCOONa$$

Intramolecular Cannizzaro reaction given by dialdehydes having no α-hydrogen.

Perkin condensation

CHO

O

O

H

CH3-C-O-C-CH3

CH3COONa

$$180^{\circ}C$$

OH

CH-CH2COOCOCH3

CH=CH-COOH

$$\frac{H^{+}/\Delta}{-H_{2}O}$$

Cinnamic acid

Benzoin condensation

Reformatsky reaction

$$R = C + Br - CH_{2}COOC_{2}H_{5} \xrightarrow{Zn/ether reflux}$$

$$R = C + Br - CH_{2}COOC_{2}H_{5} \xrightarrow{Zn/ether reflux}$$

$$R = C + Br - CH_{2}COOC_{2}H_{5}$$

$$CH_{2}O + Br - CH_{2}COOC_{2}H_{5}$$

$$CH_{2} - C - OC_{2}H_{5}$$

CARBOXYLIC ACIDS

Introduction

Organic compounds containing -COOH as the functional group are called carboxylic acids. The -COOH group which itself is made up of a carbonyl group (C=O) and a hydroxyl group (-OH) is called carboxyl group (*carb* from carbonyl and *oxyl* from hydroxyl).

Carboxylic acids may be aliphatic or aromatic according to the -COOH group which is attached to an alkyl group (or a hydrogen atom) or an aryl group. Their general formulae are:

$$R-C$$
 O $Ar-C$ O

Aliphatic carboxylic acid Aromatic carboxylic acid (where R = H or any alkyl group) (where Ar is any aryl group)

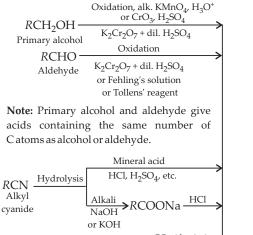
 $\label{eq:General}$ General formula : $C_nH_{2n}O_2$

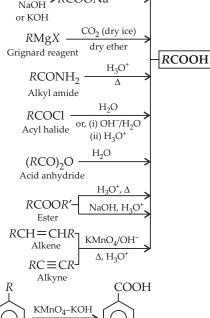
CLASSIFICATION

Nomenclature

- The longest chain containing the carboxylic group (-COOH) is selected.
- The carbon chain is numbered from the carboxylic acid group and the carboxylic carbon is always given the number one.
- While writing IUPAC name of carboxylic acid 'e' of alkane is replaced by 'oic' acid.

Preparation





Benzoic acid

	MPP-6	CLA	SS XI		1A	VSW	ER	KEY	
1.	(b)	2.	(d)	3.	(c)	4.	(a)	5.	(a)
6.	(d)	7.	(c)	8.	(d)	9.	(a)	10.	(c)
11.	(a)	12.	(d)	13.	(c)	14.	(a)	15.	(b)
16.	(d)	17.	(a)	18.	(a)	19.	(d)	20.	(a,b)
21.	(a,b,c,d)	22.	(a,b)	23.	(a,c)	24.	(5)	25.	(4)
26.	(4)	27.	(d)	28.	(d)	29.	(a)	30.	(d)

Alkyl benzene

PHYSICAL PROPERTIES

Physical properties

Physical state: The lower fatty acids upto C_9 are colourless liquids. The higher ones are colourless waxy solids.

Odour: The first three members have a sharp pungent odour. The middle ones, C₄ to C₉, have an odour of rancid butter. The higher members do not possess any smell.

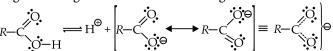
Boiling points: Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses due to more extensive association of their molecules through intermolecular hydrogen bonding. The H-bonds are not broken completely even in the vapour phase.

Solubility: Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water.

CHEMICAL PROPERTIES

Acidic nature

Carboxylic acids are weaker acids than mineral acids but they are stronger acids than alcohols and many simple phenols. The carboxyl group and carboxylate anion are stabilised by resonance, however, the stabilisation of anion will be much more than that of carboxylic acid. The carboxylate ion is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative atom.



Carboxylate anion



Effect of substituents on acidic strength

Electron withdrawing groups (*EWG*'s) make acids stronger.

$$G \leftarrow C \longrightarrow H^{\oplus} + G \leftarrow C \bigcirc C$$

Electron withdrawing group
(EWG)

Stabilizes the carboxylate anion, increases acidity

Electron donating groups (*EDG*'s) make acids weaker.

$$G \rightarrow C$$
 $\longrightarrow C$
 \longrightarrow

Electron donating group Destabilizes the carboxylate anion, (EDG) decreases acidity

→ -I effect increases with increasing number of EWG's. e.g.,

 $F_{3}CCOOH > F_{2}CHCOOH$ Strongest $> FCH_{2}COOH > CH_{3}COOH$

I effect decreases with increasing distance from the EWG. e.g.,

$$\begin{array}{ccc} \text{CH}_3\text{CH}_2\text{-CH}-\text{COOH} > \text{CH}_3\text{CH}-\text{CH}_2\text{-COOH} \\ & & \text{F} & \text{F} \\ & & \text{Strongest} & & \text{FCH}_2\text{CH}_2\text{-COOH} \end{array}$$

+R effect decreases the acidity and -R effect increases the acidity. *e.g.*,

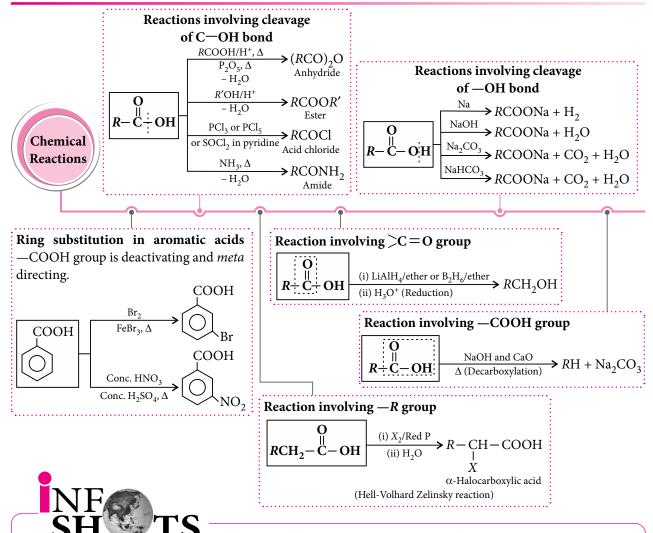
COOH COOH COOH COOH

NO₂ Cl CH₃ OCH₃

$$-I,-R$$
 $-I,+R$ $-R$ $+I$ $+R$

Because of a slight -R effect from the aromatic ring itself, benzoic acids are more acidic than alkanoic acids.

$$Ar$$
— $COOH > R$ — $COOH$



Molecular Mechanisms of Aldehydes Toxicity!

To explain the toxicity of aldehydic compounds which are electrophilic in nature and to which humans are pervasively 上 exposed, HSAB theory has been used to profile the different aldehyde subclasses with respect to electronic character electrophilic reactivity and biological nucleophilic targets. Analysis indicated that short chain aldehydes and longer chain saturated alkanals are hard electrophiles that cause toxicity by forming adducts with hard biological nucleophiles, e.g., primary nitrogen groups on lysine residues. In contrast, α, β-unsaturated carbonyl derivatives, alkenals and the α -oxoaldehydes are soft electrophiles that preferentially react with soft nucleophilic thiolate groups on cysteine residues. Thus, toxic potencies of these are generally related to corresponding electrophilicities. But for some aldehydes, predictions of toxicity based on electrophilicity are less accurate due to inherent physicochemical variables that limit target accessibility, e.g., steric hindrance and solubility. The unsaturated aldehydes are also members of the conjugated type-2 alkene chemical class that includes, α , β -unsaturated amide, ketone, and ester derivatives. Type-2 alkenes are electrophiles of varying softness and electrophilicity that share a common mechanism of toxicity. Therefore, exposure to an environmental mixture of unsaturated carbonyl derivatives could cause "type-2 alkene toxicity" through additive interactions. Finally, we propose that environmentally derived aldehydes can accelerate diseases by interacting with endogeneous aldehyde generated during oxidative stress. This review provides a basis for understanding aldehyde mechanisms and environmental toxicity through the context of electronic structure, electrophilicity, and nucleophile target selectivity.

SPEED PRACTICE

- 1. Which of the following reactions gives the compound,

 - (d) None of these
- **2.** In the following reaction sequence the correct structures of *E*, *F* and *G* are

$$Ph \xrightarrow{O O \\ *} OH \xrightarrow{Heat} [E] \frac{I_2}{NaOH} [F] + [G]$$

(* implies ¹³C labelled carbon)

(a)
$$E = \bigcup_{Ph}^{O} F = \bigcup_{Ph}^{O} - G = CHI_3$$

(b)
$$E = \bigcup_{Ph}^{O} \bigcup_{CH_3}^{*} F = \bigcup_{Ph}^{O} \bigcup_{ONa}^{+} G = CHI_3$$

(c)
$$E = \bigcup_{Ph}^{O} {\star \atop CH_3} F = \bigcup_{Ph}^{O} {-+\atop ONa} G = {\star \atop CHI_3}$$

(d)
$$E = \bigcup_{Ph}^{O} \underset{CH_3}{\overset{*}{\underset{}}} F = \bigcup_{Ph}^{O} \underset{O}{\overset{*}{\underset{}}} Ha$$

- **3.** The correct statement regarding a carbonyl compound with a hydrogen atom on its alphacarbon, is
 - (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
 - (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its

- corresponding enol and this process is known as keto-enol tautomerism
- (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
- (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

(NEET Phase - I 2016)

4. From the given set of reactions,

$$A \xrightarrow{\text{(i) NaOI}} B \xrightarrow{\text{Heat}} C$$

Starting compound A corresponds to

(a)
$$O$$
 CH_2COOH
(b) CH_2COOH
(c) O
 $COCH_3$
(d) O
 $COCH_3$

5. Identify *A* in the following reaction,

$$C_6H_6 \xrightarrow{A, AlCl_3} Acetophenone$$

- (a) CH₃COCl
- (b) C₆H₅COCl
- (c) CH₃CHO
- (d) SO₂Cl₂
- **6.** The correct structure of the product '*A*' formed in the reaction

$$\frac{\text{O}}{\text{H}_2 \text{ (gas, 1 atmosphere)}} A \text{ is}$$

(NEET Phase - II 2016)

- 7. Which of the following reagents would distinguish *cis*-cyclopenta-1,2-diol from the *trans*-isomer?
 - (a) MnO_2
- (b) Aluminium isopropoxide
- (c) Acetone
- (d) Ozone

(NEET Phase - I 2016)

- 8. H.V.Z reaction involves the use of P and Cl₂ CH₃CH₂COOH P,Cl₂ → CH₃CHClCOOH The function of phosphorus is
 - (a) as a catalyst
 - (b) in the formation of PCl_3 which carries out halogenation at the α -carbon atom
 - (c) in the formation of PCl₃ which converts —COOH into —COCl
 - (d) none of these.
- **9.** Which of the following calcium salt will give cyclopentanone on heating?
 - (a) Calcium succinate (b) Calcium adipate
 - (c) Calcium glucarate (d) Calcium oxalate
- **10.** The correct statement(s) about the following reaction sequence is(are)

reaction sequence is(are)
$$Cumene(C_9H_{12}) \xrightarrow{(ii) O_2} P \xrightarrow{CHCl_3/} Q + R \atop (Major) + (Minor)$$

$$Q \xrightarrow{NaOH} S$$

- (a) R is steam volatile
- (b) *Q* gives dark violet colouration with 1% aqueous FeCl₃ solution
- (c) *S* gives black precipitate with 2, 4-dinitrophenyl hydrazine
- (d) *S* gives dark violet colouration with 1% aqueous FeCl₃ solution. (JEE Advanced 2016)
- **11.** Which of the following will not undergo Cannizzaro reaction on heating with an alkali solution?
 - (a) CCl₃CHO
- (b) (CH₃)₃CCHO
- (c) HCHO
- (d) C_6H_5CHO
- 12. Oxidation of toluene with CrO₃ in the presence of (CH₃CO)₂O gives a product (A) which on treatment with aqueous NaOH produces
 - (a) C₆H₅CHO
- (b) $(C_6H_5CO)_2O$
- (c) C₆H₅COONa
- (d) C_6H_5OH
- **13.** The correct order of acidity for the following compounds is:

- (a) I > II > III > IV
- (b) III > I > II > IV
- (c) III > IV > II > I
- (d) I > III > IV > II

(JEE Advanced 2016)

- 14. In the following reactions,
 - (i) $CH_3CH_2ONa \xrightarrow{CO, \Delta} A$
 - (ii) $CH_2=CH_2 + CO + H_2O \xrightarrow{H_3PO_4} B$ A and B respectively are
 - (a) CH₃CH₂COOH in both cases
 - (b) CH₃CH₂CHO in both cases
 - (c) CH₃CH₂COOH, CH₃CHO
 - (d) CH₃CHO, CH₃COOH
- **15.** The correct statement about the synthesis of erythritol (C(CH₂OH)₄) used in the preparation of PETN, is
 - (a) the synthesis requires three aldol condensations and one Cannizzaro reaction
 - (b) alpha hydrogens of ethanol and methanol are involved in this reaction.
 - (c) the synthesis requires two aldol condensations and two Cannizzaro reactions.
 - (d) the synthesis requires four aldol condensations between methanol and ethanol.

(JEE MAIN 2016 Online)

(d) both (a) and (b).

16. The product/s in the following sequence of reactions is/are

$$(a) \xrightarrow{\text{RCO}_3 \text{H}} (A) \xrightarrow{\text{(i) LiAlH}_4/\text{ether}} \text{Product/s}$$

$$(b) \xrightarrow{\text{OH}} (b)$$

17. The reagents employed to carry the following transformation are

$$\begin{array}{cccc}
O & & & & & & & \\
O & O & & & & & & \\
O & O & & & & & & \\
H_{3}C & CH_{3} & & & & & \\
\end{array}$$

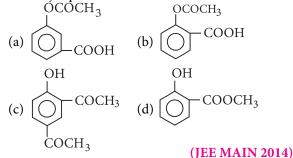
(a) LiAlH₄, H₂SO₄/heat

(c) >-OH

- (b) PCC/CH₂Cl₂ followed by HIO₄
- (c) NaBH₄/CH₃OH followed by HIO₄
- (d) O_3 followed by $(CH_3)_2S$
- **18.** Sodium phenoxide when heated with CO₂ under pressure at 125°C yields a product which on acetylation produces *C*.

$$ONa + CO_2 \xrightarrow{125^{\circ}C} B \xrightarrow{H^+} CO_2 \xrightarrow{125^{\circ}C} B$$

The major product *C* would be



19. Consider the reaction,

$$CH_3-C-OH+CH_3CH_2OH \xrightarrow{H^+} A+B$$

A and B respectively are

(a)
$$CH_3 - C - OC_2H_5 + H_2O$$

O
(b) $CH_3 - C - OC_2H_5 + H_2O^1$
O
(c) $CH_2 - C - OC_2H_5 + H_2O^1$

20. Which of the following combination of reagents

can brought transformation?

(d) both (a) and (b

$$CH_2Br$$
 CH_2OCH_3
 Br
 $COOH$

(a) CH₃ONa, Mg/ether, CO₂,H₂O/H⁺

(b) CH₃ONa, KCN/DMSO, H₂O/H₂SO₄ heat

(c) Mg/ether, CO₂,H₂O/H⁺, CH₃ONa

(d) NaOH, Mg/ether, CO₂, H₂O/H⁺,CH₃I

21.
$$\bigcirc$$
 O $\xrightarrow{\text{NaOH, }\Delta}$ A. 'A' can be

22. In a set of the given reactions, acetic acid yielded a product C

Product
$$C$$
 $CH_3COOH + PCl_5 \longrightarrow A \xrightarrow{C_6H_6} B \xrightarrow{C_2H_5MgBr} C$

Product C would be

(a) $CH_3 - C(OH)C_6H_5$ (b) $CH_3CH(OH)C_2H_5$

(c) CH₃COC₆H₅

(d) $CH_3CH(OH)C_6H_5$

23. The correct order of decarboxylation of the three acids is:

24. An ester A with molecular formula $C_9H_{10}O_2$ was treated with excess of CH3MgBr and the complex so formed was treated with H₂SO₄ to give an olefin B. Ozonolysis of B gave a ketone with molecular formula C₈H₈O which shows +ve iodoform test. The structure of A is

(a) C₆H₅COOC₂H₅

(b) CH₃COCH₂COC₆H₅

(c) p-CH₃O $-C_6$ H₄-COCH₃

(d) $C_6H_5COOC_6H_5$

25. Which alkene is formed from the following reaction $CH_3CH_2CH_2CH=PPh_3 + 2 - Butanone?$

(a) 3-methyl-3-heptene (b) 4-methyl-3-heptene

(c) 5-methyl-3-heptene (d) 5-methylheptane

26. The relative reactivities of acyl compounds towards nucleophilic substitution are in the order of

(a) acid anhydride > amide > ester > acyl chloride

(b) acyl chloride > ester > acid anhydride > amide

(c) acyl chloride > acid anhydride > ester > amide

(d) ester > acyl chloride > amide > acid anhydride

27.
$$CH_3CCH_2CH_2COCH_2CH_3 \xrightarrow{\text{(i) } CH_3MgBr \\ \text{(one mole)}} A$$
,

A formed in this reaction is

OH O
| II
(a)
$$CH_3CCH_2CH_2COCH_2CH_3$$

 CH_3

c)
$$H_3C$$
 O CH_3 CH_3 CH_3 CH_3 $CH_2CH_2CCH_3$ CH_3 CH_3

28. Acetal formation is a reversible reaction

$$\begin{array}{c} \stackrel{R}{\longrightarrow} \text{C=O} + R'\text{OH} \stackrel{\text{H}^+}{\longleftarrow} \stackrel{R}{\longrightarrow} \text{C} \stackrel{\text{OH}}{\searrow} \stackrel{R'\text{OH}, \text{H}^+}{\longleftarrow} \\ \stackrel{R}{\longrightarrow} \text{C} \stackrel{\text{OR}'}{\searrow} + \text{H}_2\text{O} \end{array}$$

Under what conditions, the reaction can be forced to proceed only in right (forward) direction?

- (a) Using excess of alcohol
- (b) Using high temperature
- (c) Using dilute acid and excess of alcohol
- (d) Using dry acid and excess of alcohol
- **29.** Which one of the following pairs is not correctly matched?

(a)
$$>$$
C=O $\xrightarrow{\text{Clemmensen's reduction}} >$ CH₂

(b)
$$>$$
C=O $\xrightarrow{\text{Wolff-Kishner reduction}} >$ CHOH

(c)
$$-COC1 \xrightarrow{Rosenmund's reduction} -CHO$$

(d)
$$-C \equiv N \xrightarrow{\text{Stephen's reduction}} -CHO$$

30. Which of the following is most stable, and which one is least?

- (a) III is most stable and I is least
- (b) IV is most stable and I is least
- (c) III is most stable and IV is least
- (d) All the four are equally stable

SOLUTIONS

- (c): (a) Nitration is difficult to be carried out, further the —NO₂ group will go to *m*-position to the C=O group.
 - (b) Nitrobenzene, being deactivated toward electrophilic substitution will not undergo Friedal Craft reaction.
 - (c) Benzene easily undergoes Friedal Craft reaction forming the required product.

2. (d): Ph * OH Heat Ph
$$\stackrel{\star}{E}$$
 CH₃ $\stackrel{I_2}{NaOH}$ OPh $\stackrel{-}{E}$ NaOH Ph $\stackrel{-}{E}$ ONa + $\stackrel{\star}{C}$ H₃

3. (b): Keto-enol tautomerism :

$$\begin{array}{c|c}
 & C \\
 & C \\$$

4. (c): Given reagents indicate the presence of $-\text{COCH}_3$ group in the starting compound *A*. Further, since the -COOH group introduced in *B* due to iodoform reaction is absent in the final product, *B* should be a β-keto acid. Hence, *A* should have structure given in option (c).

$$\begin{array}{c}
O \\
COCH_3
\end{array}
\xrightarrow{(i) \text{NaOI}}$$

$$\begin{array}{c}
O \\
COOH
\end{array}
\xrightarrow{(-CO_2)}$$

$$\begin{array}{c}
O \\
COOH
\end{array}$$

5. (a):
$$\langle \underline{\hspace{0.2cm}} \rangle$$
 + CH₃COCl $\xrightarrow{\text{AlCl}_3}$ $\langle \underline{\hspace{0.2cm}} \rangle$ Acetophenone

6. (b)

7. (c):
$$OH + O = C CH_3 -H_2O CH_3$$

cis-cyclopenta-1,2-diol Acetone OCH_3
 CH_3

Trans-isomer does not react with acetone.

8. (c)

9. (b):
$$CH_2CH_2CO$$
 Ca $CaCO_3 + CaCO_3 + CaCO_3 + Colcium adipate $Calcium adipate$ $Cyclopentanone$$

10. (b)

11. (a): Although CCl₃CHO does not contain α-hydrogen, yet it does not undergo Cannizzaro reaction since attack of OH⁻ ion cleaves the molecule to give CHCl₃ and HCOO⁻

$$CCl_3$$
- $CHO \xrightarrow{OH^-} CCl_3$ - $CH \xrightarrow{O^-} OH$

$$CHCl_3 + HCOO^- \longleftarrow [CCl_3^- + HCOOH]$$

12. (a)

13. (a): Due to *ortho*-effect, (I) and (II) are stronger acid than (III) and (IV). Due to two *ortho* hydroxyl groups in (I), it is stronger acid than (II). (III) is a stronger acid than (IV) because at *m*-position, –OH group cannot exert its +*R* effect but can only exert its -*I* effect while at *p*-position, –OH group exerts its strong +*R* effect.

Thus, the correct order of acidity is:

I > II > III > IV

14. (a): (i) CH₃CH₂ONa
$$\xrightarrow{\text{CO, }\Delta}$$
 under pressure

CH₃CH₂COONa
$$\xrightarrow{\text{dil. HCl}}$$
 CH₃CH₂COOH

(ii) CH₂=CH₂ + CO + H₂O $\xrightarrow{\text{H_3PO_4} \atop \text{under pressure}}$

A and *B* both are propionic acid.

18. (b)

19. (d): Consider the acid catalysed mechanism of esterification:

$$\begin{array}{c} O \\ CH_{3}-C-OH \xrightarrow{H^{+}/CH_{3}CH_{2}OH} & OH \\ CH_{3}-C-OH \xrightarrow{H^{+}/CH_{3}CH_{2}OH} & CH_{3}-C-OH \\ & & +OCH_{2}CH_{3} \\ & & +OH_{2} & :OH \\ \hline \\ Proton transfer & CH_{3}-C-OH_{2} & OCH_{2}CH_{3} \\ & & +OH_{2} & :OH \\ \hline \\ Proton transfer & OCH_{2}CH_{3} & OCH_{2}CH_{3} \\ & & -H^{+} \uparrow \downarrow -H_{2}O & -H^{+} \uparrow \downarrow -H_{2}O^{18} \\ & & -H^{+} \uparrow \downarrow -H_{2}O & -H^{+} \uparrow \downarrow -H_{2}O^{18} \\ & & -H^{+} \uparrow \downarrow -H_{2}O & OCH_{2}CH_{3} \\ & & +OH_{3}-C-OH_{2}CH_{3} & OCH_{2}CH_{3} \\ \hline \\ & & +OH_{3}-C-OH_{2}CH_{3} & OCH_{2}CH_{3} \\ & +OH_{3}-C-OH_{2}CH_{3} & OCH_{2}CH_{3} \\ & +OH_{3}-C-OH_{2}CH_{3} & OCH_{2}CH_{3} \\ & +OH_{3}-C-OH_{3}-C-OH_{2}CH_{3} \\ & +OH_{3}-C-OH_{2}CH_{3} & OCH_{2}CH_{3} \\ & +OH_{3}-C-OH_{3}-C-OH_{3} & OCH_{2}CH_{3} \\ & +OH_{3}-C-OH_{3}-C-OH_{3} \\ & +OH_{3}-C-OH_{3} \\ & +O$$

20. (a):
$$CH_2Br$$
 CH_2OCH_3
 Br CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CH_2OCH_3
 CO_2
 CO_2
 CO_2
 CO_3
 CO_3

23 . (b): β -Keto carboxylic acids and β , γ -unsaturated carboxylic acids undergo decarboxylation easily because the corresponding carbanion is quite stable due to resonance.

$$\begin{array}{c} O \\ CH_{3}-C-CH_{2}-COOH \xrightarrow{-H^{+}} \\ CH_{3}-C-CH_{2}-COOH \xrightarrow{-H^{+}} \\ CH_{3}-C-CH_{2}-C \xrightarrow{-CO_{2}} \\ CH_{3}-C-CH_{2} \longleftrightarrow CH_{3}-C-CH_{2} \xrightarrow{+H^{+}} \\ OH & O \\ CH_{3}-C-CH_{2} \longleftrightarrow CH_{3}-C-CH_{3} \\ \end{array}$$

CH₃CH=CHCH₂
$$\overset{O}{-CO_2}$$

 CH_3 CH=CH $\overset{O}{-CH_2}$ $\overset{O}{-CO_2}$
 CH_3 CH=CH $\overset{O}{-CH_2}$ $\overset{O}{-CO_2}$
 CH_3 CH=CH $\overset{O}{-CH_2}$ $\overset{O}{-CO_2}$
 CH_3 CH=CH=CH₂ $\overset{O}{-CO_2}$

$$CH_2 = \stackrel{O}{CH} - \stackrel{O}{C} \stackrel{-CO_2}{\longrightarrow} CH_2 = \stackrel{-}{CH}$$

24 (a): Since ketone with M.F. C₈H₈O shows +ve iodoform test, therefore, it must be a methyl ketone, *i.e.*, C₆H₅COCH₃. This ketone is obtained by the ozonolysis of an olefin *B* which is obtained by the addition of excess of CH₃MgBr to ester *A*. The reactions can be given as:

reactions can be given as:
$$\begin{array}{c} C_{6}H_{5}-COOC_{2}H_{5} \xrightarrow{i.2CH_{3}MgBr} C_{6}H_{5}-COOH_{2} \\ A(M.F., C_{9}H_{10}O_{2}) \end{array} \\ \begin{array}{c} C_{1}H_{3} \\ C_{2}H_{3} \\ C_{3}H_{2}O -H_{2}SO_{4} \\ CH_{3} \\ CH_{3$$

- 25. (a) 26. (c)
- 27. (c)
- **28.** (d): Being reversible reaction, the backward reaction *i.e.*, acetal hemiacetal step can be restricted by minimizing water content, *i.e.*, by using dry HCl. The step hemiacetal aldehyde can be restricted by using excess of alcohol.
- 29. (b) 30. (c)



ACE YOUR W

Biomolecules, Polymers and Chemistry in Everyday Life

GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.
- 1. Which of the following is a natural polymer? Buna-S, Proteins, PVC
- 2. State two functions of carbohydrates.
- 3. Which class of drugs is used in sleeping pills?
- **4.** Which category of the synthetic detergents is used in toothpaste?
- 5. Is $-(NH-CHR-CO)_{\overline{n}}$, a homopolymer or copolymer?
- **6.** Write the name of monomers used for getting the following polymers :
 - (i) Bakelite
 - (ii) Neoprene
- 7. How are synthetic detergents better than soaps?

OR

How do antiseptics differ from disinfectants? Give one example of each.

8. What are essential and non-essential amino acids? Give two examples of each type.

Previous Years Analysis								
	201	6	201	5	2014			
	Delhi A		Delhi	Al	Delhi	Al		
VSA –		_	_	-	1	_		
SA-I	_	-	_	_	_	_		
SA-II	2	2	2	2	2	2		
VBQ	1	1	1	1	1	1		
LA	_	_	_	_	_	_		

Time Allowed: 3 hours Maximum Marks: 70

- Write any two reactions of glucose which could not be explained by open chain structure of glucose molecule.
- **10.** Explain the difference between polyacrylates and polyesters.
- **11.** Write the name of monomers of the following polymers.

(i)
$$\begin{bmatrix} H & H & O & O \\ I & I & II \\ N - (CH_2)_6 - N - C - (CH_2)_4 - C \end{bmatrix}_n$$

(ii)
$$\begin{bmatrix} O & H \\ || & || \\ C - (CH_2)_5 - N \end{bmatrix}_n$$

- (iii) $\{-CF_2-CF_2-\}_n$
- 12. Account for the following.
 - (i) Some builders are added to soap.
 - (ii) Using soap is safer than detergents from the environmental point of view.
 - (iii) Ethanol is added to soaps.

- **13.** (i) Mention the biological importance of insulin.
 - (ii) Write the important structural and functional differences between DNA and RNA.
- **14.** Write the names and structures of the monomers of the following polymers.
 - (i) Buna-S
 - (ii) Buna-N
 - (iii) Dacron
- 15. Mention one use for each of the following drugs:
 - (i) Ranitidine
 - (ii) Paracetamol
 - (iii) Tincture of iodine.
- **16.** Define the following terms as related to proteins :
 - (i) Peptide linkage
 - (ii) Primary structure
 - (iii) Denaturation

OR

- (i) What type of bonding helps in stabilisation of α -helix structure of proteins?
- (ii) Differentiate between globular and fibrous proteins.
- **17.** (i) Give a best known example of polyester used as a synthetic fibre.
 - (ii) Name the compounds from which this polyester is prepared.
 - (iii) What type of polymerisation takes place during the formation of this polyester from these compounds?
- **18. (i)** Write the chemical equation for preparing sodium soap from glyceryl palmitate and glyceryl oleate. Structural formulae of these compounds are given below.
 - (a) $(C_{15}H_{31}COO)_3C_3H_5$ Glyceryl palmitate (b) $(C_{17}H_{33}COO)_3C_3H_5$ — Glyceryl oleate
 - (ii) If soap has high alkali content, it irritates skin. How can the amount of excess alkali be determined? What can be the source of excess alkali?
- **19.** (i) What is the scientific explanation for the feeling of depression?
 - (ii) What is the mode of action of antimicrobial drugs?
 - (iii) What is the medicinal use of narcotic drugs?

- **20.** (i) During curdling of milk, what happens to sugar present in it?
 - (ii) Why must vitamin C be supplied regularly in diet?
 - (iii) Amino acids behave like salts rather than simple amines or carboxylic acids. Explain.
- **21.** (i) Define thermoplastics.
 - (ii) State the significance of numbers 6 and 6, 6 in the polymer names nylon-6 and nylon 6, 6.
- **22.** Account for the following:
 - (i) Aspirin drug helps in the prevention of heart attack.
 - (ii) Diabetic patients are advised to take artificial sweeteners instead of natural sweeteners.
 - (iii) Detergents are non-biodegradable while soaps are biodegradable.
- 23. The judicial system in our country is quite slow. Sometimes it takes 10-15 years to decide a criminal or a rape or a paternity case. Pragya, a class XII student, pointed out that recent developments in forensic sciences has evolved DNA fingerprinting technique which is quite fast and gives reliable results

After reading the above passage, answer the following questions:

- (i) What is DNA fingerprinting and how DNA fingerprinting has been useful in identification of criminals?
- (ii) How DNA fingerprinting has been used to determine the paternity of a person?
- (iii) Can DNA fingerprinting be used to prove someone innocent?
- 24. (i) Name two fat soluble vitamins, their sources and the diseases caused due to their deficiency in diet.
 - (ii) What is essentially the difference between α -form and β -form of glucose? Explain.
 - (iii) What is meant by biocatalysts?
 - (iv) Write a reaction which shows that all the carbon atoms in glucose are linked in a straight chain.

OR

- (i) What is isoelectric point?
- (ii) What is mutarotation?

- (iii) B-complex is an often prescribed vitamin. What is complex about it and what is its usefulness?
- (iv) Except for vitamin B_{12} , all other vitamins of group B, should be supplied regularly in diet. Why?
- (v) Fresh tomatoes are a better source of vitamin C than those which have been stored for some time. Explain.
- **25.** (i) Write the mechanism of free radical polymerisation.
 - (ii) Identify the monomer in the following polymeric structures.

(a)
$$\begin{bmatrix} O & O \\ \parallel & \parallel \\ C - (CH_2)_8 - C - NH - (CH_2)_6 - NH \end{bmatrix}_n$$
(b)
$$\begin{bmatrix} N & NH - CH_2 \\ N & NH \end{bmatrix}$$

(iii) What are biodegradable polymers? Give one example.

OR

- (i) Which one is the prefered method to polymerize acrylonitrile, anionic or cationic polymerisation? Explain your choice.
- (ii) A regular copolymer of ethylene and vinyl chloride contains alternate monomers of each type. What is the weight percent of ethylene in this copolymer?
- 26. (i) Both antacids and antiallergic drugs are antihistamines but they cannot replace each other. Explain why?
 - (ii) What is the commonality between the antibiotic arsphenamine and azodye?
 - (iii) What is the harmful effect of hyperacidity?

OR

- (i) Explain the role of allosteric site in enzyme inhibition.
- (ii) Name two α -amino acids which form a dipeptide which is 100 times more sweet than cane sugar.
- (iii) Hair shampoos belong to which class of synthetic detergent?

SOLUTIONS

- 1. Proteins are natural polymers.
- (i) Carbohydrates act as storage molecules like starch in plants and glycogen in animals.
 - (ii) They act as a constituent of cell membranes of plants and bacteria.
- 3. Tranquilizers are used in sleeping pills.
- 4. Anionic detergents are used in toothpastes.
- 5. Since, the unit $(NH-CHR-CO)_n$ is obtained from the single monomer unit $NH_2-CHR-COOH$, hence, it is a homopolymer.
- 6. (i) Bakelite : Formaldehyde (HCHO) and Phenol (C_6H_5OH)
 - (ii) Neoprene : $CH_2 = C CH = CH_2$ Chloroprene
- 7. (i) They can work well even with hard water without any wastage while some of the soap gets wasted in hard water.
 - (ii) They can be used in acidic as well as mineral water.

OR

Antiseptics are those chemicals which are not harmful to the living tissues but suppress the growth of microorganisms, *e.g.*, dettol, savlon, 0.2% phenol, tincture of iodine, etc.

Disinfectants are used to kill microorganisms in drains, toilets, sick rooms, etc. They are harmful for the living tissues, *e.g.*, KMnO₄, bleaching powder, 1% solution of phenol, etc.

- **8.** Essential amino acids are those amino acids which must be part of our diet. They are not synthesised by our body, *e.g.*, valine, leucine, isoleucine, phenylalanine, etc.
 - Non-essential amino acids are those amino acids which are produced in our body, *e.g.*, glycine, alanine, serine, cysteine, etc.
- 9. Open chain structure of glucose molecule cannot explain the following:
 - (i) Glucose does not react with sodium bisulphite (NaHSO₃) to form addition product though it has aldehyde group.

- (ii) Glucose does not give Schiff's test and 2, 4-DNP test like other aldehydes.
- 10. Polyacrylates are formed from the esters of acrylic acid ($CH_2 = CHCOOH$), such as $CH_2 = CHCOOR$. For example, polymethyl methacrylate (PMMA),

These are addition polymers. They are formed by chain growth polymerisation.

Polyesters are polymers having ester linkages

O || (-C-O-R). Dicarboxylic acids and diols undergo condensation polymerisation to form polyesters, *e.g.*, terylene (Dacron fibre), glyptal.

- 11. Monomers of polymers
 - (i) Hexamethylene diamine and adipic acid
 - (ii) Caprolactam
 - (iii) Tetrafluoroethene
- 12. (i) Builders like sodium carbonate and trisodium phosphate are added to soap as water softeners. They make the soaps action more rapid. They function by precipitating problematic ions of water.
 - (ii) Soaps are biodegradable while detergents contain branched hydrocarbons that are quiet stable, *i.e.*, they do not degrade by the action of microorganisms and therefore, cause water pollution in rivers.
 - (iii) Ethanol is added to soaps to make them transparent.
- **13.** (i) Controls the metabolism of glucose in the body and maintains glucose level in the blood.
 - (ii) **Structural differences**: The main structural differences between DNA and RNA are as follows:
 - (a) The sugar moiety present in DNA is β -D-2-deoxyribose, whereas in RNA molecule, it is β -D-ribose.
 - (b) DNA has a double stranded helical structure, while RNA has a single stranded helical structure.
 - (c) DNA contains cytosine and thymine as pyrimidine base, whereas RNA has cytosine and uracil as pyrimidine bases. Functional difference: DNA controls the transmission of hereditary character while RNA controls the synthesis of proteins.

- 4. (i) 1,3-Butadiene (CH₂=CH-CH=CH₂) and styrene $\begin{pmatrix} CH = CH_2 \\ C_6H_5 \end{pmatrix}$
 - (ii) 1,3-butadiene ($CH_2 = CH CH = CH_2$) and acrylonitrile ($CH_2 = CHCN$).
 - (iii) Ethylene glycol (HO—H₂C—CH₂—OH) and terephthalic acid or Benzene-1, 4-dicarboxylic acid.

$$\begin{pmatrix} O & O \\ \parallel & \parallel \\ HO-C- & \end{pmatrix} - C-OH \end{pmatrix}$$

- 15. (i) Ranitidine is used as an antacid.
 - (ii) Paracetamol is used to bring down the body temperature during high fever.
 - (iii) Tincture of iodine is used as an antiseptic. It is 2-3% solution of iodine in alcohol and water.
- 16. (i) Proteins are the polymers of α -amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond e.g.,

$$\begin{bmatrix} -NH - CH - C - NH - CH - C - \\ R \end{bmatrix}$$
Peptide linkage

- (ii) Primary structure: The specific sequence in which the various amino acids present in a protein are linked to one another is called its primary structure. Any change in the primary structure creates a different protein.
- (iii) Denaturation: The loss of biological activity of a protein by changing the pH, temperature or by adding some salt due to disruption of the native structure of protein is called denaturation.

During denaturation secondary and tertiary structure of protein is destroyed but primary structure remains intact.

OR

- (i) Hydrogen bonding.
- (ii) Characteristic differences between globular and fibrous proteins can be given as:

S. No.	Globular proteins	Fibrous proteins
1.	These are cross- linked proteins and are condensation product of acidic and basic amino acids.	These are linear condensation polymer.
2.	These are soluble in water, mineral acids and bases.	These are insoluble in water but soluble in strong acids and bases.
3.	These proteins have three dimensional folded structure. These are stabilised by internal hydrogen bonding, e.g., egg albumin, enzymes.	by intermolecular

- **17.** (i) Terylene is a polyester which is used as a synthetic fibre.
 - (ii) Terylene is a polymer of ethylene glycol and terephthalic acid.

$$n$$
HO $-$ CH $_2$ $-$ CH $_2$ $-$ OH $+$ n HO $-$ C $-$ OH $-$ Ethylene glycol

$$\begin{bmatrix}
O & O & O \\
O & CH_2 - CH_2 - O - C
\end{bmatrix}$$
Terylene (Dacron)
$$\begin{bmatrix}
O & O & O \\
O & C & C
\end{bmatrix}$$

$$\begin{bmatrix}
-nH_2O & C & C
\end{bmatrix}$$

(iii) Condensation polymerisation takes place during the formation of the polyester from terephthalic acid and ethylene glycol.

18. (i) (a)
$$CH_2-O-C-C_{15}H_{31}$$
 $CH-O-C-C_{15}H_{31} + 3NaOH$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-O-C-C_{15}H_{31}$
 $CH_2-C-C_{15}H_{31}$
 CH_2-C-C_2
 C

(b) O | CH₂-O-C-C₁₇H₃₃ | O | CH-O-C-C₁₇H₃₃ + 3NaOH
$$\stackrel{\text{Heat}}{-}$$
 | O | CH₂-O-C-C₁₇H₃₃ or (C₁₇H₃₃COO)₃C₃H₅ Glyceryl oleate | CH₂OH | CHOH + 3C₁₇H₃₃COONa | Sodium oleate | CH₂OH | Glycerol

- (ii) Acid-base titration, *i.e.*, titrating a soap solution with standard HCl using a phenolphthalein as indicator, can be used to determine the excess amount of alkali in soap. The excess alkali left after hydrolysis of oil can be the source of alkalinity in soap.
- 19. (i) Noradrenaline is a neuro-transmitter which plays an crucial role in mood changes. If any person has low level of noradrenaline, then the message transfer process becomes slow and the person feels depressed.
 - (ii) An antimicrobe tends to destroy/prevent development or inhibit the pathogenic action of microbes such as bacteria, fungi, virus or other parasites selectively. Thus, antimicrobial are drugs which cure diseases caused by microorganisms.
 - (iii) Narcotic analgesics (morphine and many of its homologous) when administered in medicinal doses, relieve pain and produce sleep. They are chiefly used for the relief of postoperative pain, cardiac pain and pains of terminal cancer, and in child birth.
- **20.** (i) During curdling of milk lactose (sugar) is transformed to lactic acid by the action of enzyme 'lactase' present in bacteria.
 - (ii) Vitamin C is water soluble hence, they are regularly excreted in urine and can not be stored in our body, so, they must be supplied regularly in diet.
 - (iii) Amino acids have acidic COOH group as well as NH₂ group hence, COOH looses its H to NH₂, hence they exist as Zwitter ion and behave like salt.

- 21. (i) Polymers which can be repeatedly softened on heating and hardened on cooling and can be used again and again without any change in their chemical composition and mechanical strength are called thermoplastics. For example, polythene, teflon, polystyrene, etc.
 - (ii) Nylon 6 means that it is a condensation polymer of only one type of monomer molecules containing six carbon atoms, i.e., caprolactam. Nylon 6, 6, on the other hand, implies that it is a condensation polymer of two types of monomer molecules each containing six carbon atoms, i.e., adipic acid (HOOCCH₂CH₂CH₂CH₂COOH) and hexamethylenediamine (H₂N(CH₂)₆NH₂)
- **22.** (i) Most of the heart attacks are due to blood clotting in the coronary arteries. Aspirin helps to make the blood thinner and thus prevents the formation of blood clots in the coronary arteries thereby preventing heart attacks.
 - (ii) Diabetic patients do not produce enough insulin to metabolise the natural sugar. As a result, sugar remains in the blood and thus affects, liver, heart and kidneys. Therefore, diabetic patients are advised to take artificial sweeteners such as saccharin. It is not metabolised in the body and is excreted as such through urine.
 - (iii) Soaps have straight hydrocarbon chains which are easily degraded by bacteria present in the sewage water and hence do not cause water pollution. On the other hand, detergents have branched hydrocarbon chains which are either not attacked or attacked only slowly by bacteria. As a result, detergents remain undegraded in rivers and waterways and thus cause water pollution.
- 23. (i) Every person has his own unique fingerprints. Like fingerprints, each person's DNA is unique. Any cell from skin, blood, semen, saliva, etc. can supply the DNA samples for analysis. The fingerprints from the site of crime are collected and then amplified. These fingerprints are then

- compared with the DNA fingerprints of all the suspects and of other people known to have been present at the scene or the site of crime. A perfect match of fingerprints identifies the criminal.
- (ii) Since children inherit half of their DNA from each parent, therefore, DNA fingerprinting has been used to establish the parentage of a child of contested biological origin.
- (iii) DNA fingerprinting has been useful in proving suspected people innocent. If the DNA fingerprint does not match, the suspected person is innocent.
- **24.** (i) Examples of fat soluble vitamins are vitamin A and D.

Name of vitamins	Sources	Deficiency diseases
Vitamin A	Fish liver oil, carrots, butter, milk	Night blindness
Vitamin D	Fish and egg yolk	Rickets and osteomalacia

(ii) In α-D-Glucose, the -OH group at C₁ is towards right whereas in β-D-glucose, the -OH group at C₁ is towards left. Such a pair of stereoisomers which differ in the configuration only at C₁ are called anomers.

- (iii) Substances which catalyse chemical reactions taking place in living organisms are called biocatalysts, *e.g.*, enzymes.
- (iv) Glucose when heated with red P and HI gives *n*-hexane.

$$C_6H_{12}O_6 \xrightarrow{\text{Red P, HI}} CH_3CH_2CH_2CH_2CH_3$$
n-Hexane

It indicates presence of straight chain of six carbon atoms in glucose.

- (i) The pH at which there is no net migration of the amino acid under the influence of an applied electric field is called isoelectric point. For example, the isoelectric point of glycine is 6.1, that of aspartic acid is 3.0 and that of lysine is 9.7.
- (ii) The spontaneous change of specific rotation of an optically active substance with time is called mutarotation. For example, when a freshly prepared solution of α -D-glucose is allowed to stand. Its specific rotation decreases from + 111° to + 52.5° with time and that of β -Dglucose increases from + 19.2° to +52.5°.
- (iii) It is a group of vitamins which contains vitamins B₁, B₂, B₆, B₁₂, biotin, pantothenic acid (Vitamin B₅), folic acid and nicotinic acid (Vitamin B₃). Since it is not a single vitamin but is a group of vitamins, that is why, it is called vitamin B-complex. It is required to release energy from food and to promote healthy skin and muscles. Its deficiency causes beriberi (Vitamin B₁) and pernicious anaemia (Vitamin B_{12}).
- (iv) Vitamin-B₁₂ does not occur in plants but is exclusively synthesised by the microorganisms present in the body. Therefore, it may not be supplied regularly in diet, while all other vitamins of group B should be supplied regularly in diet.
- (v) On prolonged exposure to air, vitamin C present in tomatoes is destroyed due to aerial oxidation.
- Chain initiation:

$$\dot{R} + H_2 \dot{C} = \dot{C}H_2 \longrightarrow R - CH_2 - \dot{C}H_2$$

Chain propagation:

$$R-CH_2-\dot{C}H_2+CH_2=CH_2 \longrightarrow$$

$$R - CH_2 - CH_2 - CH_3 - \dot{C}H_3$$

Chain termination:

$$R-CH_2-CH_2-CH_2-\dot{C}H_2+\dot{R} \longrightarrow$$

O O
$$\parallel$$
 \parallel (a) HO-C-(CH₂)₈-C-OH and

Decane-1, 10-dioic acid

$$H_2N - (CH_2)_6 - NH_2$$

Hexamethylenediamine

(iii) Biodegradable Polymers : The natural polymer, which disintegrates by itself or by microorganisms within certain period of time is called biodegradable polymer, e.g., PHBV (poly-β-hydroxybutyrate-co-βhydroxyvalerate), Nylon-2-nylon 6.

Acrylonitrile ($CH_2 = CH - CN$) contains an electron withdrawing cyano (— $C \equiv N$) group which can stabilise a carbanion intermediate. Since in anionic polymerisation, carbanion intermediates are produced both in the initiation step as well as in the chain propagation step, therefore, polymerisation of acrylonitrile must be carried out under anionic conditions.

$$\begin{array}{c} NH_2^+ + CH_2 = CH \longrightarrow H_2N - CH_2 - CH_2 \longrightarrow N \\ Amide ion & CN & C \longrightarrow N \\ Acrylonitrile & Stabilised by -R-effect of the - CN group \\ H_2N - CH_2 - CH & C \longrightarrow N \end{array}$$

Chain-propagation step:

Chain-propagation step:

$$H_2NCH_2$$
— CH : $+CH_2$ — CH
 CN
 CN
 H_2N-CH_2 — $CH-CH_2$ — CH :

 CN
 $C=N$:

Stabilised by- R -effect of the $-CN$ group

(ii) The structure of the copolymer is $n \text{ CH}_2 = \text{CH}_2 + n \text{ CH}_2 = \text{CHCl}$ $(-CH_2CH_2CH_2CHCl -)_n$ Mol. wt. of ethylene = 28

Mol. wt. of vinyl chloride = 62.5

Empirical formula wt. of copolymer

=28 + 62.5 = 90.5

Wt. percent of ethylene in the copolymer

$$=\frac{28}{90.5}\times100=30.94$$

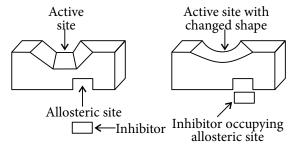
- 26. (i) Histamine is a chemical substance that stimulates the secretion of pepsin and hydrochloric acid in stomach. Antacids are designed to prevent the interaction of histamine with the receptors present in the stomach wall. As a result, less HCl is released in stomach. Histamine contracts the smooth muscles in the bronchi and gut and relaxes other muscles in walls of fine blood vessels. As a result, histamine causes allergy. Antihistamines interfere with the natural action of histamine by competing with histamine for binding sites of receptor where histamine exerts its effect. Since, antiallergic and antacids drugs work on different receptors, therefore, antacids and antiallergic drugs cannot replace each other.
 - (ii) Arsphenamine is also known as salvarsan. It is a synthetic organic arsenic compound that was previously used for treating syphilis. Arsphenamine possess As As linkage. Azo dyes are used to promote epithelial growth in the treatment of ulcers, burns, and other wounds. Many azodyes have anticoagulation action. Azo dyes possess N = N linkage like arsphenamine which possess As As linkage.

(iii) Hyperacidity produces sudden stomach pain. It may lead to vomiting, loss of appetite, flatulence and heart burn. It is also responsible for chronic indigestion and in severe cases cause gastric ulcers.

OR

(i) Some drugs do not bind to the active site of enzymes to inhibit their activities. These bind to a different site of enzyme. This binding of inhibitor (drug) changes the shape of the active site in such a way that substrate cannot recognise it. The site different from active site of an enzyme where a drug molecule can bind is called the allosteric site.

Non-competitive inhibitor changes the active site of enzyme after binding at allosteric site.



(ii) Aspartame is the most successful and widely used artificial sweetener. It is methyl ester of dipeptide formed from aspartic acid and phenylalanine. Its use is limited to cold foods and soft drinks because it is unstable at cooking temperature.

Structure of aspartame is

$$\begin{array}{c|c} O & O & O \\ II & II \\ HO-C-CH_2-CH-C-NH-CH-C-OCH_3 \\ \hline NH_2 & CH_2 \\ \hline Aspartic acid part & Phenylalanine \\ (methyl ester part) \end{array}$$

(iii) Hair shampoos are made up of cationic detergents. These are quarternary ammonium salts of amines with acetates, chlorides or bromides as anions, *e.g.*, cetyltrimethyl ammonium bromide.

$$\begin{bmatrix} \text{CH}_{3} \\ \text{H}_{3}\text{C} - (\text{CH}_{2})_{15} - \overset{|}{\text{N}} - \text{CH}_{3} \\ \text{CH}_{3} \end{bmatrix}^{+} \text{Br}^{-}$$

Cetyltrimethyl ammonium bromide



EXAMINE



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.					
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.					
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.					
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.					
Section - V	 Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as: (a) If both assertion and reason are true and reason is the correct explanation of assertion. (b) If both assertion and reason are true but reason is not the correct explanation of assertion. (c) If assertion is true but reason is false. (d) If both assertion and reason are false. 					
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).					

CHEMICAL KINETICS

SECTION - I

Only One Option Correct Type

- The rate of a gaseous reaction is halved when the volume of the vessel is doubled. The order of reaction is
 - (a) 0
- (b) 1
- (c) 2
- (d) 3
- 2. In the first order reaction, the concentration of the reactant decreases from 800 mol/dm³ to 50 mol/dm³ in 2×10^4 sec. The rate constant of the reaction in sec^{-1} is
 - (a) 2×10^4
- (b) 3.45×10^{-5}
- (c) 1.386×10^{-4}
- (d) 2×10^{-4}
- The rate of a first order reaction is $0.04 \text{ mol } L^{-1} \text{ s}^{-1}$ at 10 minutes and 0.03 mol L⁻¹ s⁻¹ at 20 minutes after initiation. The half-life of the reaction is
 - (a) 4.408 min
- (b) 44.086 min
- (c) 24.086 min
- (d) 2.408 min
- The rate constant of a reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C. Evaluate the Arrhenius parameter A.
 - (a) 45.2×10^7
- (b) 54.2×10^{10}
- (c) 4.52×10^9
- (d) 5.42×10^{10}

- For the reaction, $Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$, the initial concentration of I was 0.20 mol L and the concentration after 20 min was 0.18 mol L⁻¹. Then, the rate of formation of I_2 in mol L^{-1} min⁻¹ would be
 - (a) 1×10^{-3}
- (b) 5×10^{-4}
- (c) 1×10^{-4}
- (d) 5×10^{-3}
- When inversion of sucrose is studied at pH = 5, the half life period is always found to be 500 minutes irrespective of any initial concentration but when it is studied at pH = 6, the half-life period is found to be 50 minutes. The rate law expression for the inversion of sucrose is
 - (a) Rate = k [Sucrose][H⁺]⁰
 - (b) Rate = $k[Sucrose][H^+]$
 - (c) Rate = $k[Sucrose][H^+]^3$
 - (d) Rate = $k[Sucrose][H^+]^2$
- The following mechanism has been proposed for the reaction of NO with Br₂ to form NOBr;

$$NO_{(g)} + Br_{2(g)} \xrightarrow{fast} NOBr_{2(g)}$$

 $NOBr_{2(g)} + NO_{(g)} \xrightarrow{slow} 2NOBr_{(g)}$

If the second step is the rate determining step, the order of the reaction with respect to $NO_{(g)}$ is

- (a) 1
- (b) 0
- (c) 3
- (d) 2

- 8. Under the same reaction conditions, initial concentration of 1.386 mol dm⁻³ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order
 - (k_1) and zero order (k_0) of the reaction is
 - (a) $0.5 \text{ mol}^{-1} \text{ dm}^3$
- (b) 1.0 mol dm^{-3}
- (c) 1.5 mol dm^{-3}
- (d) $2.0 \text{ mol}^{-1} \text{ dm}^3$
- 9. Cyclopropane, C₃H₆ rearranges to form propene, CH_3 — $CH = CH_2$
 - This follows first order kinetics. The rate constant is $2.714 \times 10^{-3} \text{ sec}^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec?
 - (a) 0.035 M
- (b) 0.22 M
- (c) 0.145 M
- (d) 0.0018 M
- **10.** For a reaction, $A + B \rightarrow C + D$, if the concentration of *A* is doubled without altering the concentration of B, the rate gets doubled. If the concentration of B is increased by nine times without altering the concentration of A, the rate gets tripled. The order of the reaction is
 - (a) 2
- (b) 1
- (c) $\frac{3}{2}$ (d) $\frac{4}{3}$

SECTION - II

More than One Options Correct Type

- 11. Which of the following statements are correct?
 - (a) A plot of $\log k$ versus $\frac{1}{T}$ is linear.
 - (b) A plot of log[X] versus time is linear for a first order reaction $X \rightarrow P$.
 - (c) A plot of log P versus $\frac{1}{T}$ is linear at constant volume.
 - (d) A plot of P versus $\frac{1}{V}$ is linear at constant temperature.
- 12. Esterification of acetic anhydride by ethanol takes place as

$$(CH_3CO)_2O + C_2H_5OH \longrightarrow CH_3COOC_2H_5 \\ + CH_3COOH$$

Select the correct statements of the following.

(a) When reaction is carried out in dilute hexane solution, the rate law is given by *k* [Anhydride][Alcohol].

- (b) When ethanol is the solvent, the rate law is given by k[Anhydride].
- (c) The value of *k* in the two cases are same.
- (d) Using ethanol as the solvent, its concentration changes significantly during the course of the reaction.
- 13. In acidic medium, the rate of reaction between [BrO₃] and Br⁻ ions is given by the expression.

$$-\frac{d[BrO_3^-]}{dt} = k[BrO_3^-][Br][H^+]^2$$

- (a) rate constant of the reaction depends upon the concentration of H⁺ ions
- (b) rate of reaction is independent of concentration of acid added
- (c) the change in pH of the solution will affect the rate of reaction
- (d) doubling the concentration of H⁺ ions will increase the reaction rate by 4 times.

SECTION - III

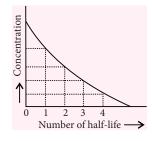
Paragraph Type

Paragraph for Questions 14 and 15

The half-life of a reaction is the time required for the concentration of reactant to decrease by half, i.e.,

$$[A]_t = \frac{1}{2}[A]$$

$$t_{1/2} = \frac{0.693}{k}$$



this means $t_{1/2}$ is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.

- 14. 75% of a reaction of the first order was completed in 32 min. Find the half-life of the reaction.
 - (a) 8 min (b) 16 min (c) 64 min (d) 48 min
- 15. The rate of a first order reaction is 1.5×10^{-2} mol L⁻¹ min⁻¹ at 0.5 M concentration of the reactant. The half-life of the reaction is
 - (a) 13.6 min
- (b) 42.5 min
- (c) 23.1 min
- (d) 32.5 min

Paragraph for Questions 16 and 17

In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction.' Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.

- **16.** For an elementary reaction $2A + B \longrightarrow 3C$, the rate of appearance of 'C' at time 't' is 1.3×10^{-4} mol L⁻¹ s⁻¹. Rate of reaction at time 't' will be
 - (a) $\frac{1}{2}(1.3 \times 10^{-4}) \text{ mol } L^{-1} \text{ s}^{-1}$
 - (b) $\frac{2}{3}(1.3\times10^{-4}) \text{ mol } L^{-1} \text{ s}^{-1}$
 - (c) $1.3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - (d) $\frac{1}{3}$ (1.3×10⁻⁴) mol L⁻¹ s⁻¹
- 17. The rate constant of a reaction is found to be $3 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$. The order of the reaction is
 - (a) 0.5 (b) 2

List I

- (c) 3
- (d) 1

List II

SECTION - IV

Matching List Type

18. Match the entries of List I with appropriate entries of List II and select the correct answer using the codes given below the lists:

	(React	ions)				(Order of reaction)
P.	2HI –	H_2	+ I ₂		1.	1
Q.	2 N ₂ O ₅	$\longrightarrow 4$	$NO_2 + 0$	O_2	2.	2
R.	CH ₃ C		3.	1.5		
	CH_3	COO	$+ C_2H_5C$	H		
S.	$H_2 + B$	$r_2 \longrightarrow$	2HBr		4.	0
	P	Q	R	S		
(a)	2	4	1	3		
(b)	4	1	2	3		
(c)	1	2	3	4		
(d)	2	1	4	3		

19. Match the entries of List I with appropriate entries of List II and select the correct answer using the codes given below the lists:

List I	List II
(Plot)	(Slope of the line)

- P. Concentration *vs* time for zero order reaction
- 1. *k*
- Q. Half-life period *vs* initial concentration for zero order reaction
- 2. -k
- R. Reciprocal of concentration *vs* time for second order reaction
- $3. \quad \frac{1}{2k}$
- S. Half-life period *vs* initial concentration for first order reaction
- 4. zero
- **P Q R S** (a) 3 2 1 4
- (b) 2 3 1 4
- (c) 4 3 1 2
- (d) 1 2 3 4

SECTION - V

Assertion Reason Type

20. Assertion: For a chemical reaction with rise in temperature by 10 °C, the rate constant is nearly doubled.

Reason : At t + 10 the fraction of molecules having energy equal to or greater than activation energy gets doubled.

21. Assertion : The reactions, $2NO + O_2 \longrightarrow 2NO_2$ and $2CO + O_2 \longrightarrow 2CO_2$ proceed at the same rate because they are similar.

Reason: Both the reactions have the same activation energy.

22. Assertion : 50% of a zero order reaction is completed in 100 sec, therefore, 75% reaction will be completed in 150 sec.

Reason : The rate constant of a zero order reaction depends upon time.

Integer Value Correct Type

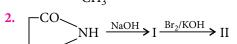
- 23. An organic compound undergoes first-order decomposition. The time taken for its decomposition to $\frac{1}{8}$ and $\frac{1}{10}$ of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$?
- 24. The rate constant of a zero order reaction is 3×10^{-3} mol L⁻¹s⁻¹. The time taken in seconds for the initial concentration of reactant to fall from 0.10 M to 0.076 M will be
- **25.** For a first order reaction, the number of half-lives required for the initial concentration of the reactant to fall to 3.125% of its initial concentration is

AMINES AND BIOMOLECULES

SECTION - I

Only One Option Correct Type

- 1. An organic compound 'A' on treatment with NH₃ gives 'B' which on heating gives 'C', 'C' when treated with Br₂ in the presence of KOH produces ethylamine. Compound 'A' is
 - (a) CH₃COOH
- (b) CH₃CH₂CH₂COOH
- (c) CH₃-CHCOOH
- (d) CH₃CH₂COOH



In the above sequence, II is

- (a) β-alanine
- (b) α-alanine
- (c) ethylenediamine
- (d) γ-aminobutyric acid.
- 3. Consider the following sequence of reactions,

Glucose
$$\xrightarrow{\text{C}_6\text{H}_5\text{NHNH}_2} X \xrightarrow{\text{dil.HCl}} Y \xrightarrow{\text{Zn/CH}_3\text{COOH}} Z$$

The final product (Z) is

- (a) sorbitol
- (b) fructose
- (c) mannose
- (d) mannitol.
- 4. α Maltose consists of
 - (a) one $\alpha\text{-D-glucopyranose}$ unit and one $\beta\text{-D-glucopyranose}$ unit with 1, 2-glycosidic linkage
 - (b) two α -D-glucopyranose units with 1,2-glycosidic linkage
 - (c) two β -D-glucopyranose units with 1,4-glycosidic linkage
 - (d) two α -D-glucopyranose units with 1,4-glycosidic linkage.
- **5.** Which of the following amines cannot be prepared by Gabriel phthalimide reaction?
 - (a) Benzylamine
- (b) Aniline
- (c) Ethylamine
- (d) Methylamine
- **6.** A compound 'A' has a molecular formula, C₇H₇NO. Ontreatmentwith Br₂ and KOH, 'A' gives an amine 'B'

- which gives carbylamine test. 'B' upon diazotisation and coupling with phenol gives an azo dye. 'A' can be
- (a) C₆H₅CONHCOCH₃
- (b) $C_6H_5CONH_2$
- (c) $C_6H_5NO_2$
- (d) o-, m- or p-C₆H₄(NH₂)CHO
- 7. Which of the following does not reduce C₆H₅NO₂ to aniline?
 - (a) Sn/HCl
- (b) SnCl₂/HCl
- (c) Zn/HCl
- (d) LiAlH₄
- **8.** Which of the following statements is true?
 - (a) Epimers are also anomers.
 - (b) Anomers are also epimers.
 - (c) Both of the above statements are true.
 - (d) None of the above statements is true.
- 9. The product of reaction between chloroform and ethanamine in presence of alcoholic KOH is allowed to react with Na/C₂H₅OH. The final product is
 - (a) ethyl chloride
- (b) ethylene dichloride
- (c) N-methylethanamine
- (d) ethanal.
- **10.** The hormone which controls the processes of burning of fats, proteins and carbohydrates to liberate energy in the body is
 - (a) cortisone
- (b) adrenaline
- (c) thyroxine
- (d) insulin.

SECTION - II

More than One Options Correct Type

11. The correct statements about the following sugar *X* and *Y* are

- (a) X is a reducing sugar and Y is a non-reducing sugar
- (b) X is a non-reducing sugar and Y is a reducing sugar
- (c) the glycosidic linkages in X and Y are α and β respectively
- (d) the glycosidic linkages in X and Y are β and α respectively.
- 12. Which of the following can exist as an inner salt?
 - (a) p-Aminobenzenesulphonic acid
 - (b) *p*-Aminobenzoic acid
 - (c) Aminoacetic acid (d) Alanine
- 13. The compound 'X' with molecular formula $C_4H_{11}N$ on treatment with HNO_2 gives a tertiary alcohol with molecular formula $C_4H_{10}O$. The compound 'X' will give
 - (a) carbylamine reaction
 - (b) Hofmann mustard oil reaction
 - (c) diazonium salt as intermediate with HNO₂
 - (d) gives 2-methyl-2-nitropropane on oxidation with $KMnO_4$.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

A mixture of two compounds 'A' and 'B' was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound 'A', when heated with alcoholic solution of KOH produced a compound 'C' (C_7H_5N) associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compound 'D' and 'E' of molecular formula, $C_7H_6O_7$.

- **14.** Compounds *A* and *B* respectively are
 - (a) C_6H_5OH , $C_6H_5OCH_3$
 - (b) $C_6H_5NH_2$, C_6H_5OH
 - (c) C_6H_5OH , $C_6H_5NH_2$
 - (d) C₆H₅CH₂OH, C₆H₅CH₂NH₂

- **15.** The compounds *D* and *E* respectively are
 - (a) C_6H_5CHO , o-HO— C_6H_4CHO
 - (b) C_6H_5CHO , m-HO— C_6H_4CHO
 - (c) C_6H_5CHO , p-HO— C_6H_4CHO
 - (d) o-HO— C_6H_4 CHO, p-HO— C_6H_4 CHO

Paragraph for Questions 16 and 17

Polynucleotides are called nucleic acids. Each nucleotide is made up of three parts, *i.e.*, a pentose sugar, a heterocyclic nitrogenous base and phosphoric acid. Depending upon the nature of sugar whether, ribose or 2-deoxyribose, nucleic acids are called RNA and DNA respectively. In all, there are five nitrogenous bases, two of which are purines while the remaining three are pyrimidines. Out of these five bases, each type of nucleic acid has four of them.

- **16.** Which of the following sets of bases are present both in DNA and RNA?
 - (a) Adenine, uracil, thymine
 - (b) Adenine, guanine, cytosine
 - (c) Adenine, guanine, uracil
 - (d) Adenine, guanine, thymine
- **17.** In nucleic acids, the nucleotides are linked to one another through
 - (a) hydrogen bond
- (b) peptide bond
- (c) glycosidic linkage
- (d) phosphate groups.

SECTION - IV

Matching List Type

18. Match the entries of List I with appropriate entries of List II and select the correct answer using the codes given below the lists:

	List I				List II
P.	CH ₃ CI	H ₂ NH ₂		1.	Undergoes Liebermann nitrosoamine reaction
Q.	$C_6H_5NH_2$			2.	Undergoes Hofmann bromamide reaction
R.	$(CH_3)_2$	NH		3.	Gives azo dye test
S.	CH ₃ CONH ₂			4.	With alcoholic KOH and $CHCl_3$ produces bad smell
	P	Q	R		S
(a)	4	3	1		2
(b)	3	4	1		2
(c)	2	3	1		4
(d)	1	2	3		4
	Q. R. S. (a) (b) (c)	P. CH ₃ CH Q. C ₆ H ₅ N R. (CH ₃) ₂ S. CH ₃ CO P (a) 4 (b) 3 (c) 2	P. $CH_3CH_2NH_2$ Q. $C_6H_5NH_2$ R. $(CH_3)_2NH$ S. CH_3CONH_2 P Q (a) 4 3 (b) 3 4 (c) 2 3	P. $CH_3CH_2NH_2$ Q. $C_6H_5NH_2$ R. $(CH_3)_2NH$ S. CH_3CONH_2 P Q R (a) 4 3 1 (b) 3 4 1 (c) 2 3 1	P. $CH_3CH_2NH_2$ 1. Q. $C_6H_5NH_2$ 2. R. $(CH_3)_2NH$ 3. S. CH_3CONH_2 4. P Q R (a) 4 3 1 (b) 3 4 1 (c) 2 3 1

19. Match the entries of List I with appropriate entries of List II and select the correct answer using the codes given below the lists:

List I

List II

- Glycosidic linkage
- 1. Globular protein
- Q. Maltase
- Connects monosaccharide units
- Peptide bond
- 3. Monomeric unit of nucleic acids
- Nucleotide

(d) 1

Connects two amino acid units

P	Q	R	S
(a) 4	3	2	1
(b) 3	4	1	2
(c) 2	1	4	3

2

SECTION - V

4

3

Assertion Reason Type

20. Assertion : Reduction of *m*-dinitrobenzene with ammonium sulphide gives *m*-nitroaniline.

Reason: m-Nitroaniline formed gets precipitated and hence further reduction is prevented.

21. Assertion: A solution of sucrose in water is dextrorotatory but on hydrolysis in presence of little hydrochloric acid, it becomes laevorotatory.

Reason: Sucrose on hydrolysis gives unequal amounts of glucose and fructose as a result of which change in sign of rotation is observed.

22. Assertion: Oxidation of 1-nitronaphthalene gives 3-nitrophthalic acid whereas 1-amino-naphthalene on oxidation gives phthalic acid.

Reason: An amino group attached to the benzene ring makes it resistant to oxidation whereas nitro group makes the benzene ring susceptible to oxidation.

SECTION - VI

Integer Value Correct Type

23. How many of the following amines are more basic than aniline? o-toluidine, m-toluidine, p-toluidine, p-anisidine, *m*-anisidine. p-aminophenol, o-anisidine.

m-aminophenol, *o*-aminophenol.

- 24. A decapeptide (Mol. wt. 796) on hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is
- 25. A tetrapeptide has —COOH group on alanine and produces glycine (Gly), valine (Val), phenylalanine (Phe) and alanine (Ala) on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with -NH2 group attached to a chiral center is

SOLUTIONS

CHEMICAL KINETICS

- **(b)**
- (c): Let the concentrations of the reactant after 10 min and 20 min be C_1 and C_2 respectively.

.. rate after 10 min =
$$k.C_1$$

= $0.04 \times 60 \text{ mol L}^{-1}\text{min}^{-1}$
and rate after 20 min = $k.C_2$
= $0.03 \times 60 \text{ mol L}^{-1}\text{min}^{-1}$

$$\therefore \quad \frac{C_1}{C_2} = \frac{4}{3}$$

Let the reaction starts after 10 minutes.

$$k = \frac{2.303}{10} \log \frac{C_1}{C_2} = \frac{2.303}{10} \log \frac{4}{3} = 0.02878$$

$$\therefore t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.02878} = 24.086 \text{ min}$$

- 4. (d)
- (a): At pH = 5, as half-life period is found to be independent of initial concentration of sucrose, this means with respect to sucrose, it is a reaction of first order, *i.e.*, Rate = k [Sucrose].

If *n* is the order with respect to H⁺ ion,
$$t_{1/2} \propto [\text{H}^+]^{1-n}$$
, i.e., $500 \propto (10^{-5})^{1-n}$ [pH = 5 means [H⁺] = 10^{-5} M] ...(i) and $50 \propto (10^{-6})^{1-n}$ [pH = 6 means [H⁺] = 10^{-6} M]

Dividing (i) by (ii), $10 = (10)^{1-n}$ i.e. 1 - n = 1n = 0, i.e., order with respect to H^+ ion = 0. Hence, overall rate law is Rate = $k[Sucrose] [H^+]^0$

7. (d):
$$r = k'[NOBr_2][NO]$$
 ...(i)

$$K_c = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]} \qquad \dots (ii)$$

By eqn. (i) and (ii), $r = k'K_c \cdot [NO][Br_2][NO] = k''[NO]^2[Br_2]$ Thus, order with respect to NO is 2.

(a): For first order reaction,

$$k_1 = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{0.5a} = \frac{2.303}{t_{1/2}} \log_{10} 2 = \frac{0.693}{t_{1/2}}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{k_1}$$

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$$

 $\therefore k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$ For zero order reaction, $t_{1/2} = \frac{a}{2k_0}$

$$k_0 = \frac{a}{2 \times t_{1/2}} = \frac{1.386}{2 \times 20}$$

Now, $\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{40}{1.386} = 0.5 \text{ mol}^{-1} \text{ dm}^3$

- 9. (b)
- 11. (a,b,d): Statement (c) is wrong because $P \propto T$ at constant volume.
- 12. (a,b): (a) In dilute hexane solution, concentration of both anhydride and ethanol change with the progress of the reaction and the rate depends upon the concentrations of both the reactants.
 - (b,d) When solvent (ethanol) is also a reactant, its concentration is so large in comparison to anhydride that it remains practically constant. So, the rate does not depend on [ethanol].
 - (c) The value of k are not the same in the two cases.
- 13. (c,d)
- 14. (b)
- 15. (c)

- 17. (c): Unit of k for n^{th} order = $(\text{mol L}^{-1})^{1-n} \sec^{-1}...(i)$ Here, $k = 3 \times 10^{-3} \text{ mol}^{-2} \text{ L}^2 \text{ sec}^{-1}$ Unit of $k = \text{mol}^{-2} \text{ L}^2 \text{ sec}^{-1} \Rightarrow (\text{mol L}^{-1})^{-2} \text{sec}^{-1}$...(ii) Comparing (i) and (ii) we get, $1 - n = -2 \Rightarrow n = 3$
- 18. (b)
- 19. **(b)**
- 20. (a)

- 21. (d)

23. (9):
$$\frac{t_{1/8}}{t_{1/10}} = \frac{\frac{2.303}{k} \log \frac{1}{1/8}}{\frac{2.303}{k} \log \frac{1}{1/10}}$$

$$\frac{t_{1/8}}{t_{1/10}} \times 10 = \left[\frac{\log 8}{\log 10} \right] \times 10 = 9$$

24. (8)

25. (5): Amount left after *n* half-lives, $A = \frac{|A|_0}{2^n}$ Here, $[A]_0$ is the initial amount = 100% and A is final amount = 3.125 %

Thus,
$$3.125 = \frac{100}{2^n} \implies n = 5$$

AMINES AND BIOMOLECULES

(d): CH₃CH₂COOH Propionic acid Ammonium propanoate

$$CH_{2}CH_{2}NH_{2} \xleftarrow{Br_{2}/KOH}_{\text{(Hofmann bromamide reaction)}} CH_{3}CH_{2}CONH_{2}$$

$$CH_{3}CH_{2}CONH_{2}$$

$$CH_{3}CH_{2}CONH_{2}$$

$$CH_{3}CH_{2}CONH_{2}$$

$$CH_{3}CH_{2}CONH_{2}$$

- $H_2N-CH_2-CH_2-COOH \xleftarrow{Br_2/NOT1}$ (Hofmann bromamide
- $\begin{array}{c} \text{CHO} \\ \text{H-C-OH} \xrightarrow[\text{Excess}]{C_6H_5\text{NHNH}_2} \xrightarrow[\text{Excess}]{C} = \text{NNHC}_6H_5 \end{array}$ 3. (b):

Glucose

$$CH=O \longrightarrow CH_2OH$$

$$C=O \longrightarrow (Reduction) \longrightarrow CH_2OH$$

$$R \longrightarrow R$$

$$R \longrightarrow R$$

$$Y \longrightarrow R$$
Fructose

where $R = HOCH_2(CHOH)_3$

- **(b)**
- 5. **(b)**
- **(b)**

7. (d)

- 9. (c) 10. (a)
- 11. (b,c): X has acetal linkage and Y has hemiacetal linkage. Carbohydrates with hemiacetal linkage are reducing sugars and carbohydrate with acetal linkage are non reducing sugars.

X is α - anomer and *Y* is β -anomer of D(+)-glucose.

- 12. (a,c,d): In p-NH₂C₆H₄COOH, COOH group is very weak acid so it cannot transfer H+ to the weakly basic amino group. All other three form zwitter ions.
- **13.** (a,b,c,d) : Since the compound 'X' with molecular formula C₄H₁₁N on treatment with HNO₂ gives a tertiary alcohol, therefore, (X) must be a 1° amine and as such it must give carbylamine

reaction. It undergoes oxidation with KMnO₄ to give 2-methyl-2-nitropropane and must form diazonium salt as an unstable intermediate during its reaction with HNO₂.

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{NH}_{2} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{CH}_{3} \\ \text{Namine} \\ X \\ \text{CH}_{3} \\ \text{Diazonium salt} \\ \text{(unstable)} \\ \text{CH}_{3} - \text{C} - \text{OH} \\ \text{CH}_{3} \\ \text{CH}_{3} - \text{C} - \text{OH} \\ \text{CH}_{3} \\ \text{S}^{\circ} \text{Alcohol} \\ \end{array}$$

14. (b) : Mixture of $A + B \xrightarrow{\text{CHCl}_3}$

Organic layer A + aqueous alkaline layer BSince compound A does not dissolve in alkali, therefore, it may be an amine. Further, since on treatment with CHCl3 and alcoholic KOH, it produces C (C₇H₅N) having unpleasant smell, therefore, A may be C₆H₅NH₂ and C must be C_6H_5NC and the name of the reaction is carbylamine reaction.

C₆H₅NH₂ + CHCl₃ + 3KOH(
$$alc.$$
) Warm
Aniline

A

C₆H₅NC + 3KCl + 3H₂O

Phenylisocyanide (unpleasant smell)

C

Since aqueous alkaline layer B on heating with CHCl₃ followed by acidification gives two isomeric compounds having molecular formula $(C_7H_6O_2)$. Therefore, B must be phenol, C_6H_5OH . It undergoes Reimer-Tiemann reaction to give a mixture of two isomeric compounds with molecular formula ($C_7H_6O_2$). Thus, D and E are oand *p*-hydroxybenzaldehyde.

$$C_{6}H_{5}OH \xrightarrow{CHCl_{3}/KOH} \Delta \qquad OH \\ CHO \\ O-Hydroxy- \\ benzaldehyde \qquad p-Hydroxy- \\ benzaldehyde \qquad D+E$$

15. (d)

16. (b): Adenine, guanine and cytosine are present both in DNA and RNA.

17. (d) 18. (a) 19. (c)

20. (c): The overall electron deficiency m-nitroaniline is much less (due to -R-effect of —NO₂ group and +R-effect of NH₂ group) than in m-dinitrobenzene (-R-effect of the two $-NO_2$ groups) and hence, does not accept additional electrons from a weak reducing agent such as $(NH_4)_2S$ and thus further reduction is prevented.

21. (c): Sucrose on hydrolysis gives equal amounts of glucose and fructose. Since, glucose has less positive and fructose has more negative magnitude of rotation, therefore, change in sign of rotation is observed.

22. (c)

23. (5): Due to ortho-effect, o-substituted anilines are weaker bases than aniline. However, o-aminophenol is more basic than aniline due to stabilisation of the anilinium ion by H-bonding while *m*-aminophenol is less basic than aniline due to -I-effect of the —OH group at m-position.

Thus, the five amines which are more basic than aniline are:

m- and p-toluidine; p-anisidine and o- and *p*-aminophenol.

24. (6): Mol. wt. of decapeptide = 796 No. of H₂O molecules used for hydrolysis of decapeptide = 9

i.e., Decapeptide + 9 $H_2O \longrightarrow$

Glycine + Alanine + Phenylalanine Total wt. of amino acids obtained after addition of 9 molecules of water = $796 + 9 \times 18 = 958$ Total wt. of glycine in the hydrolysed products

Total wt. of glycine in the hydrolysed produ
$$= \frac{958 \times 47}{100} = 450.26$$
But mol. wt. of glycine = 75
$$\therefore \text{ No. of glycine units in the decapeptide}$$

$$=\frac{450.26}{75}=0$$

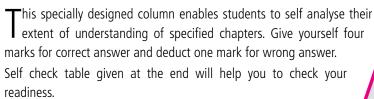
25. (4): Following combinations are possible for tetrapeptide:

Val-Phe -Gly-Ala; Val- Gly-Phe-Ala Phe -Gly -Val -Ala; Phe -Val -Gly -Ala

1. In all above sequences C-terminal is alanine.

Glycine is optically inactive amino acid, hence it should not be N-terminal so, only above combinations are possible. ��

MPP-6 MONTHLY Practice Problems



Haloalkanes and Haloarenes Alcohols, Phenols and Ethers

Total Marks: 120 Time Taken: 60 Min.

NEET / AIIMS

Only One Option Correct Type

- 1. Which of the following are arranged in the decreasing order of dipole moment?
 - (a) CH₃Cl, CH₃Br, CH₃F
 - (b) CH₃Cl, CH₃F, CH₃Br
 - (c) CH₃Br, CH₃Cl, CH₃F
 - (d) CH₃Br, CH₃F, CH₃Cl

2.
$$OCH_3 \xrightarrow{(CH_3)_3CCl} \xrightarrow{Cl_2} \xrightarrow{HBr, Heat} A$$

The final product *A*, is

3. Consider the following reaction,

$$H_{M_{h_{1}}} \rightarrow OH + SOCl_{2} \rightarrow X$$

product *X* formed is

4. Consider the following reaction sequence and identify the product, *E*.

Class XII

$$\begin{array}{c|c} CH_3 CH_3 \\ H_3C & & CH_3 \\ \hline \\ CH_3 CH_3 \end{array} \xrightarrow{\text{Na/ether}} R' - X \xrightarrow{\text{Mg}} D \xrightarrow[\text{H}_2O]{} \\ CH_3 CH_3 \end{array}$$

- (a) Propane
- (b) Butane
- (c) Isobutane
- (d) Neo-pentane
- **5.** The end product (*B*) in the following sequence of reactions is

$$CH_3Cl \xrightarrow{KCN} [A] \xrightarrow{H^+/H_2O} [B]$$

- (a) CH₃COOH
- (b) HCOOH
- (c) CH₃NH₂
- (d) CH₃COCH₃
- **6.** 1-Propanol and 2-propanol can be distinguished by
 - (a) oxidation with alkaline KMnO₄ followed by reaction with Fehling solution
 - (b) oxidation with acidic dichromate followed by reaction with Fehling solution
 - (c) oxidation by heating with copper followed by reaction with Fehling solution
 - (d) oxidation with concentrated H₂SO₄ followed by reaction with Fehling solution.

7. Which of the following compounds undergo nucleophilic substitution reaction most readily?

(a)
$$Cl \longrightarrow NO_2$$
 (b) $Cl \longrightarrow CH_3$

(c)
$$Cl$$
—OCH₃ (d) Cl —

- **8.** The reaction, $2CH_3CH_2OH \xrightarrow{H^+} CH_3CH_2OCH_2CH_3$ is believed to occur through the formation of
 - (c) $CH_3CH_2 \ddot{\ddot{O}} CH_2CH_3$ (d) all of these.
- 9. Which of the following cannot form Grignard reagent?
 - (a) CH₃CH₂Br
- (b) $CH_2 = CHBr$

(b) CH₃CH₂

(c) HC≡CCH₂Br

(a) $CH_3CH_2OH_2$

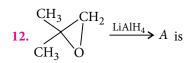
- (d) CH₂=CHCH₂Br
- 10. An organic compound 'A' reacts with sodium metal and forms 'B'. On heating with conc. H₂SO₄, 'A' gives diethyl ether. 'A' and 'B' are respectively
 - (a) C₂H₅OH and C₂H₅ONa
 - (b) C₃H₇OH and C₃H₇ONa
 - (c) CH₃OH and CH₃ONa
 - (d) C₄H₉OH and C₄H₉ONa

11.
$$R-L \xrightarrow{\text{Li}X, acetone} R-X$$

[*L* is very good leaving group].

Rate of reaction will be maximum when LiX is

- (b) LiBr (c) LiCl
- (d) LiF



- (a) (CH₃)₂CHCH₂OH (b) CH₃CH₂CH₂CH₂OH
- (c) $(CH_3)_3COH$
- (d) CH₃CHOHCH₂CH₃

Assertion & Reason Type

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.

- **13. Assertion**: Alkyl iodides darken on standing. **Reason**: Alkyl iodides are prepared by Finkelstein reaction.
- **14. Assertion :** The acidity of alcohols follows the order: $1^{\circ} > 2^{\circ} > 3^{\circ}$

Reason: +*I*-effect of the additional alkyl groups favours the cleavage of O-H bond.

15. Assertion: Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.

Reason : The reaction follows S_N1 mechanism.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. A compound (A) has molecular formula, C_7H_8O . It reacts with Na and NaOH and gives violet colour with FeCl₃, but does not decompose NaHCO₃. Upon oxidation 'A' gives 'B' which reacts with

SOLUTIONS OF NOVEMBER 2016 CROSSWORD

																	¹H										
											² A	3 M	P	Н	0	L	Y	Т	Е								
										⁴ N		U					D								⁵ K		
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										D		Ι					О								R		
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Winners of November 2016 Crossword

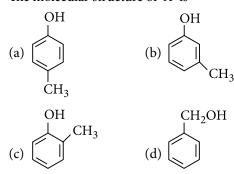
- Saumya Mehra, Mumbai
- Bhawna Joshi, West Bengal

Solution Senders of Chemistry Musing

Set - 40

- Vedika Kapoor, Bengaluru
- Debanita Mukherjee, West Bengal
- Neetu Singh, Ranchi

Na, NaOH, NaHCO3 and gives violet colour with FeCl₃. 'A' on nitration gives mononitroderivative. The molecular structure of 'A' is



17. The product obtained when

18. Identify (*C*) in the following reaction,

- (a) CH₃CHOHCH₂Cl
- (b) CH₃CHClCH₂Cl
- (c) Mixture of CH₃CHClCH₂Cl and CH₃CHOHCH₂Cl
- (d) CH₃CHClCH₂OH

19. $R_3CX + Nu^{-1}$	$\xrightarrow{\mathrm{iH}}$ NuCR ₂	+ X ⁻
$[R_3CX]$	[Nu ⁻]	$\frac{d[\text{NuC}R_3]}{dt}$
I. 0.10	0.0010	1.3×10^{-2}
II. 0.20	0.0010	2.6×10^{-2}
III. 0.10	0.0020	1.3×10^{-2}
IV. 0.30	0.0030	3.9×10^{-2}
$d[NuCR_a]$		at insignificant level, When [Nu ⁻] is increased
		also $\frac{d[\text{NuC}R_3]}{dt}$ remains
almost constar significantly. It s	nt, but —	$\frac{d[R_3CX]}{dt}$ is increasing
(a) S _N 2 compet	es now	

- (b) E2 competes now
- (c) E1 competes now
- (d) reversibility of the reaction.

More than One Options Correct Type

20. Which of the following products are obtained during the reaction,

 $Me_3CCH_2OH \xrightarrow{HBr}$

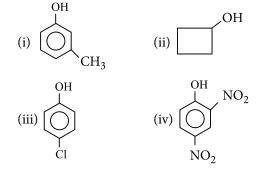
- (a) Me₃CCH₂Br
- (b) Me₂CBrCH₂CH₃
- (c) Me₃CCH₂CH₂CMe₃
- (d) Me₃CCHO
- 21. In the Liebermann test for phenols, which of the following statements are true?
 - (a) NO⁺ is the electrophile attacking on phenol.
 - (b) Tautomerization of HO--N=O takes place.
 - (c) The red colouration is due to formation of
 - (d) None of these
- **22.** The ether, \langle

when treated with HI produces

- CH_2I CH₂OH
- 23. The well known antipyretic aspirin is not obtained when
 - (a) phenol is treated with CH₃OH in presence of H_2SO_4
 - (b) salicylic acid is treated with acetic anhydride in presence of conc. H₂SO₄
 - (c) salicylic acid is treated with phenol in presence of FeCl₃
 - (d) salicylic acid is treated with acetyl chloride in presence of acid/base.

Integer Answer Type

24. Out of the following, the number of compounds which are more acidic than phenol is



(v)
$$OH$$

(vi) $CH_3CH_2CH_2OH$
 NH_2
(vii) CCl_3CH_2OH
(viii) H_2SO_4

- 25. The total number of alkenes possible by dehydrohalogenation of 3-bromo-3-cyclopentylhexane using alcoholic KOH is
- 26. In the following reaction, how many carbon atoms are there in the carbocation formed as the intermediate?

$$CH_3CH_2-O-\overset{CH_3}{\overset{|}{C}}-CH_3 \xrightarrow{HI}$$

$$CH_3$$

Comprehension Type

Alkyl halides are prepared by the addition of HX to alkenes, where alkenes are characterized by C = C bonds. As such, they are subjected to electrophilic addition reactions. Most electrophilic additions obey Markownikoff's rule. However, some exceptions are also observed. Examples of alkenes are listed below which are used for the preparation of alkyl halides.

- 27. What is the order of the compounds towards electrophilic addition of HBr?
 - (a) 2 > 4 > 1 > 3
- (b) 3 > 1 > 4 > 2
- (c) 1 > 2 > 3 > 4
- (d) 4 > 1 > 2 > 3
- 28. If solvent is water, and compound (2) is added to Br₂ the major product obtained would be

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I (Substance)

Column II (Test)

- (P) White turbidity with HCl/ZnCl₂
- (B) CH₃CH₂OH
 - (Q) Violet colour with FeCl₃

(C) CH₃-CH-Ph (R) Colour of Na₂Cr₂O₇ in presence of

 $\begin{array}{c} \text{CH}_3 \\ \text{(D) CH}_3 - \text{C-OH} \\ \text{(S)} \\ \text{CH}_3 \end{array} \quad \begin{array}{c} \text{I}_2/\text{OH}^- \\ \text{yellow ppt.} \end{array}$

30. Match the entries listed in Column I with appropriate entries listed in Column II.

S

Q

Column I

(d) R,S

Column II

- (A) (CH₃)₃CCl
- (P) Hofmann product
- (B) CH₃CH₂CH₂CH₂Cl
- (Q) Saytzeff product
- (C) CH₃CHClCH₂CH₃
- (R) E1
- (D) CH₃CHFCH₂CH₃

- (S) E2
- D

P,S

- В \mathbf{C} A
- (a) P,R S,Q Q
- (b) R
- (c) P,S Q,S
- (d) P,Q,R P,R

Keys are published in this issue. Search now! [⊙]

Check your score! If your score is

> 90% **EXCELLENT WORK!** You are well prepared to take the challenge of final exam.

90-75% GOOD WORK! No. of questions attempted You can score good in the final exam. No. of questions correct 74-60% SATISFACTORY! You need to score more next time.

Marks scored in percentage < 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

IEMISTRY MUSING

hemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. J The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PMTs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM **Set 41**

JEE MAIN/NEET

- 1. On strong heating, the acid H₅IO₆ gives (a) I_2O_4 (b) I_2O_5 (c) I_2O_7
- Consider the following reaction,

Et Me
Ph
C-COCl
$$\xrightarrow{\text{NaN}_3}$$
 $\xrightarrow{\text{Xylene}}$
A. The product A
is

Et

(a) Me
Ph
C-NH₂
(b) H₂N-C
Ph

Et

Me

(c) Me
Ph
C-CONH₂
(d) H₂NCO-C
Ph

- 3. There is a stream of neutrons with kinetic energy 0.0327 eV. If the half life of neutron is 700 sec, what fraction of neutrons will decay before they travel a distance of 100 metre? $[m_n = 1.675 \times 10^{-27} \text{ kg}]$
 - (a) 3.96×10^{-5}
- (b) 4.23×10^{-2}
- (c) 8.84×10^{-5}
- (d) 5.35×10^{-6}
- The major product obtained in the following reaction, $NC - CH = CH_2 \xrightarrow{HBr} is$
 - (a) $NC CH(Br) CH_3$
 - (b) $NC CH_2 CH_2Br$
 - (c) an equimolar mixture of (a) and (b)
 - (d) none of these.
- 5. Which of the following is correct method to convert *p*-toluidine to *p*-toluic acid?
 - (a) Diazotisation, CuCN, H₂/Pd
 - (b) CHCl₃/NaOH, KCN, Sn/HCl
 - (c) Diazotisation, CuCN/KCN, H₂O/H⁺
 - (d) Diazotisation, NaCN, NaOH

JEE ADVANCED

6. 1 g of a monobasic acid when dissolved in 100 g of water lowers the freezing point by 0.168 °C. 0.2 g of the same acid when dissolved and titrated required 15.1 mL of N/10 alkali. The degree of dissociation of the acid is (K_f is for water is 1.86)

(a) 0.19 (b) 0.29

(c) 0.11

(d) 0.21

COMPREHENSION

The shape of a molecule is determined by the number of groups of electrons around the central atom. The 'groups' might be a non-bonding single electron, a non-bonding or bonding pair of electrons, double pairs of bonding electrons or triple pairs of bonding electrons, etc. The electron 'groupings' minimise the repulsion to decrease potential energy of the system i.e., to make the Q-X-Q angle as wide as possible (X = central)atom, Q = surrounding atom).

According to VSEPR theory, repulsive interactions are summarised as lone pair – lone pair > lone pair – bond pair > bond pair - bond pair. So that as the lone pair - 'other pair' repulsion increases, the angle between these pairs increases, so the Q-X-Q angle will be slightly reduced compared to what might be expected from the simple geometry or shape.

In which of the following pairs both species have same Cl-X-Cl bond angle?

I. CCl₄, SiCl₄

II. POCl₃, SO₂Cl₂

III. BCl₃, AlCl₃

IV. SOCl₂, COCl₂

(a) I, II (b) III, II, I (c) I, III (d) II, IV

In which of the following species presence of lone pair does not affect idealised bond angle?

I. PF₃ II. BrF₃ V. XeF₂

III. IF₅

IV. ICl₄

(a) I, II, III

(b) IV, V

(c) II, V

(d) None of these

INTEGER VALUE

- 16 mL of hydrocarbon gas was exploded with excess of oxygen. On cooling, the volume of the resulting gaseous mixture was reduced by 48 mL. When KOH was added, there was a further decrease of 48 mL in the volume. The number of C-atoms in the hydrocarbon is
- **10.** For Na₂[Cr(NO)(NH₃)(C₂O₄)₂], $\mu = \sqrt{3}$ B.M. Find sum of electrons in $d_{x^2-y^2}$ and d_{z^2} orbitals of metal.





Dear students, hope you all are fine. This article is in the continuation of last month's article. Hope you will get a good grip on the isomerism part of coordination stereochemistry.

*Arunava Sarkar

\bigcirc Type 10: $M(AA)a_3b$

Logic is fix the bidentate ligand (AA) preferably at equatorial position. Now, make possible trans structure with the monodentate ligands.

So, two geometrical isomers are possible here.

Use the same logic as explained above.

$$\begin{pmatrix} A & | & b & | & a & | & b & | & b & | & a & | & b & | & a & | & b & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a & | & a$$

So, three geometrical forms are possible here.

\bigcirc Type 12: M(AA)abcd

Simple logic. Keep (AA) fixed. Now, aTb, aTc, aTd, bTc, bTd, cTd $[aTb=atranstob] <math>\therefore$ 6 geometrical forms are possible.

Note: Ma_6 , Ma_5b , $M(AA)a_4$, etc. have only one form possible.

CIS-TRANS ISOMER DETERMINATION

How to determine whether a given structure is *cis* or *trans*? We've so many techniques to determine this but, the best support is given by a bifunctional chelate group like carbonate, oxalate, ethylenediamine, etc. How? Actually, such bifunctional chelate group can occupy only 1,2-position *i.e.*, *cis* position as per the molecular dimension. So, if the substitution allows no other change in the structure then this is the *cis* isomer only which allows the chelate group to take 1,2-position.

Take the following beautiful example.

$$[Cr(en)_2Cl_2]Cl \xrightarrow{\text{Potassium}} [Cr(en)_2C_2O_4]Cl$$
Violet Oxalato complex
$$[Cr(en)_2Cl_2]Cl \xrightarrow{\text{potassium}} Fails \text{ to give}$$
Green Oxalato complex

So what do you understand from this?

The violet one is *cis* and the green one is *trans*.

But, is the above logic always true?

What if a molecular rearrangement takes place? I mean a *cis* structure converts to *trans* and *vice versa*. Sometimes this change is detectable as the *cis* and *trans* complex will have different colours.

Study of Erdmann's salt $\mathrm{NH_4[Co(NH_3)_2(NO_2)_4]}$ gives us a comparatively better idea. Erdmann's salt is prepared when air is passed through a solution of $\mathrm{CoCl_2}$ containing $\mathrm{NH_3}$, $\mathrm{NH_4Cl}$ and $\mathrm{NaNO_2}$. Now, substitution through oxalato ligands takes place here as below:

Case-1:

these two can be substituted
$$\begin{cases} O_2N & O_2N \\ O_2N & O_2N$$

Now, what does the whole scenario imply?

Actually, experimental data suggests that two compounds are obtained. So, Erdmann's salt should have *cis* structure. But, X-ray studies show that Erdmann's salt has *trans* structure. So, it is inferred that Erdmann's salt originally has got *trans* structure which during the course of the reaction has converted to *cis* structure.

Some differentiable points for identifying *cis* and *trans* isomers separately are :

- Oipole moment : cis complex has larger dipole moment than trans isomer as cis isomer lacks symmetry.
- Rate of substitution reaction: Due to the presence of the similar groups on the same side of the complex, cis isomer is found to undergo substitution reaction with a faster rate. You can use or check the following evidences.

$$\begin{array}{l} \textit{cis}[\text{Co}(\textit{en})_2\text{Cl}_2] \xrightarrow{\text{H}_2\text{O}} \textit{K} = 1.5 \times 10^{-2} \text{ min}^{-1} \\ \textit{trans}[\text{Co}(\textit{en})_2\text{Cl}_2] \xrightarrow{\text{H}_2\text{O}} \textit{K} = 2 \times 10^{-3} \text{ min}^{-1} \end{array}] 25^{\circ}\text{C}$$

O Different absorption spectra: cis and trans isomers have different absorption spectral zone. cis complex, in general, is found to have higher molar extinction coefficient. Molar extinction coefficient is the parameter which defines how strongly a substance absorbs light at a given wavelength per molar concentration.

This is also to be remembered that whether a complex will be *cis* or *trans* depends on the reaction procedure through which the complex is being produced. For example,

$$[Pt(NH_3)_4]Cl_2 + 2HCl \longrightarrow H_3N \longrightarrow Cl$$
or,
$$[Pt(NH_3)_4]^{2+} + Cl \longrightarrow [Pt(NH_3)_3Cl]^+ + NH_3$$

$$[Pt(NH_3)_3Cl]^+ + Cl \longrightarrow [Pt(NH_3)_2Cl_2] + NH_3$$

$$[Pt(NH_3)_3Cl]^+ + Cl \longrightarrow [Pt(NH_3)_2Cl_2] + NH_3$$
Similarly,
$$K_2[PtCl_4] + 2NH_3 \longrightarrow cis - [Pt(NH_3)_2Cl_2] + 2Cl \longrightarrow (PtCl_4)^{2-} + NH_3 \longrightarrow cis - [PtCl_3(NH_3)]^- + NH_3 \longrightarrow cis - [PtCl_2(NH_3)_2]$$

This is because Cl⁻ has stronger *trans* effect than NH₃.

Of course, some reactions help us to identify *cis* and *trans* isomers separately.

Now, what is *trans*-effect? According to this, a negative group coordinated to a metal atom weakens the bond of a group *trans* to it. So,

$$[Pt(NH_3)_4]Cl_2 \xrightarrow{\Delta} [Pt(NH_3)_3Cl]Cl$$

$$\downarrow^{\Delta, -NH_3}$$

$$[Pt(NH_3)_2Cl_2]$$

-Cl competes with -NH₃ to leave. So, the idea goes as below:

vanced

ACTICE PAPER

SECTION - I

(Single Correct Answer Type)

This section contains 7 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which only one is correct.

1. 17.4% (mass/V) K_2SO_4 solution at 27°C is isotonic with 5.85% (mass/V) NaCl solution at 27°C. If NaCl is 100% ionised, what is the % of ionisation of K₂SO₄ in aqueous solution?

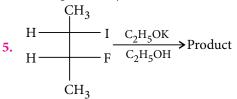
(a) 50% (b) 60%

- (c) 80% (d) 100%
- 2. XeF_{4} reacts violently with water giving a compound of Xe along with Xe, HF and O₂. The shape of the compound of Xe is
 - (a) trigonal pyramidal
 - (b) T-shape
 - (c) see-saw
 - (d) tetrahedral.
- 3. A solution of 200 mL of 1 M KOH is added to 200 mL of 1 M HCl and the mixture is well shaken. The rise in temperature T_1 is noted. The experiment is repeated by using 100 mL of each solution and rise in temperature T_2 is again noted. Which of the following is correct? (Heat of neutralisation = -13.7 kcal/equivalent)

 - (a) $T_1 = T_2$ (b) T_2 is twice as large as T_1 (c) T_1 is twice as large as T_2 (d) T_1 is four times as large as T_2
- 4. Which of the following statements is correct about the open chain product (P) obtained in the following reaction?

$$\begin{array}{c}
O \\
NH \xrightarrow{\text{(i) NaOH}} NH \xrightarrow{\text{(ii) (CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}} \xrightarrow{NH_2\text{NH}_2} P
\end{array}$$

- (a) It gives green solution on treatment with HNO₂ and then with PhOH and H₂SO₄.
- (b) It leaves a ppt. on treatment with p-toluene sulphonyl chloride.
- (c) It gives ketone on treatment with KMnO₄ and then with an acid.
- (d) It gives carbylamine test.



If the product is pure, single stereoisomer but inadequate to rotate the plane polarised light, it can be said that

- (a) the product is a mesoform
- (b) the product is an alkene formed by elimination of HF
- (c) the product is an alkene formed by elimination of HI but F is not bonded to sp² carbon
- (d) product is an alkene with F bonded to an sp^2 carbon.
- Find the incorrect statement from the following:
 - (a) The stability constant of $[Cu(NH_3)_4]^{2+}$ is greater than that of $[Cu(en)_2]^{2+}$
 - (b) Four coordinated complexes of Pd (II) and Pt (II) are diamagnetic and square planar.
 - (c) Facial and meridional isomers associated with $[Ma_3b_3]^{n+}$ type complex, both are optically
 - (d) $[CrCl_2(CN)_2(NH_3)_2]^-$ and $[CrCl_3(NH_3)_3]$ both have d^2sp^3 hybridisation
- C-14 labelled chlorobenzene is treated with NaNH,

in NH₃,
$$NaNH_2/NH_3$$

$$-33^{\circ}C$$

Which of the following depicts C-14 labelled in the products correctly?

(a)
$$NH_2$$

$$NH_2$$

$$NH_2$$

$$NH_2$$
(b) NH_2

$$NH_2$$

$$NH_3$$

$$NH_4$$

$$NH_2$$

$$NH_2$$

$$NH_2$$

$$NH_3$$

$$NH_4$$

$$NH_4$$

$$NH_5$$

$$NH_5$$

$$NH_6$$

SECTION - II

(Multiple Correct Answer Type)

This section contains 4 multiple choice questions. Each question has four choices (a), (b), (c) and (d) out of which one or more than one answer is correct.

- 8. Which of the following species will be decomposed on acidification?
 - (a) $[Ag(NH_3)_2]^+$
- (b) $[Cu(NH_3)_4]^{2+}$
- (c) $[Zn(OH)_4]^{2-}$
- (d) $[Pb(OH)_4]^{2-}$
- 9. NaH + B(OCH₃)₃ $\xrightarrow{230-270^{\circ}\text{C}}$ X + NaOCH₃

Which of the following statement(s) is/are correct?

- (a) *X* is tetrahedral in structure.
- (b) X has (3c 2e) bond.
- (c) *X* is a reducing agent.
- (d) X on reaction with water gives BO_2^- ions.
- 10. Which of the following on treatment with NaHSO₃ will produce a mixture of salts which can be separated by fractional crystallisation?

(a)
$$H_3C$$
 (b) $H-C-H$ (c) O (d) O

- 11. Which of the following processes is(are) expected to be spontaneous at higher temperature but non-spontaneous at lower temperature?
 - (a) $N_2+3H_2 \rightleftharpoons 2NH_3$ (b) $H_{2(g)} \rightleftharpoons 2H_{(g)}$ (c) $\tilde{CO_2} + \tilde{C_{(s)}} \rightleftharpoons 2\tilde{CO_{(g)}}$ $[\Delta H^{\circ}_{f}: CO_{2}^{\circ s'} = -394 \text{ kJ, } CO = -212 \text{ kJ}]$ (d) $Na_{(s)} \rightarrow Na_{(g)} + e^{-}$

(d)
$$Na_{(s)} \rightarrow Na_{(\sigma)} + e^{-}$$

SECTION - III

(Paragraph Type)

This section contains 2 paragraphs. Based upon one of the paragraphs 2 multiple choice questions and based on the other paragraph 3 multiple choice questions have to be answered. Each of these questions has four choices (a), (b), (c) and (d), out of which only one is correct.

Paragraph for Q. No. 12 and 13

For the reaction, $2A + B_2 \rightarrow 2AB$, following observations were obtained:

Rate of disappearance of B_2	[A]	$[B_2]$
$(\text{mol } L^{-1} s^{-1})$	$(mol L^{-1}$) (mol L^{-1})
1.8×10^{-3}	0.015	0.15
1.085×10^{-2}	0.090	0.15
5.4×10^{-3}	0.015	0.45

- **12.** The order of the reaction is
 - (a) zero
- (c) 2
- (d) 3
- **13.** The rate of formation of *AB* when
 - [A] = 0.02 and $[B_2] = 0.04$ mol L⁻¹ is
 - (a) 3.2×10^{-2}
- (b) 2.4×10^{-3}
- (c) 0.21×10^{-3} (d) 1.28×10^{-3}

Paragraph for Q. No. 14 to 16

$$\begin{array}{c}
\text{Ph} & \xrightarrow{\text{Cl}_2} X \\
\text{CH}_3 & \xrightarrow{\text{Cl}_2} Y
\end{array}$$

14. Compounds *X* and *Y* respectively are

(a)
$$Cl$$
 Ph and CH_2Cl CH_2Cl

(b)
$$\begin{array}{c} Ph \\ CH_2Cl \end{array}$$
 and $\begin{array}{c} Cl \\ CH_3 \end{array}$

(c)
$$Ph$$
 and CH_2CI CH_3

(d)
$$CI$$
 CH_3 and CH_3 CH_3

15. If product *X* is treated with AlCl₃, it undergoes an intramolecular Friedel-Crafts reaction and gives M. M is

16. Compound,

$$M \xrightarrow{\text{Br}_2/\text{UV light}} Z \xrightarrow{\text{(ii) Mg/Ether} \\ \text{(Mono bromo product)}} (\text{iii) CH}_2\text{O} \xrightarrow{\text{(iiii)} \text{H}_3\text{O}^+}$$

Stable product. Identify the stable product.

SECTION - IV

(Integer Answer Type)

This section contains 6 integer type questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9.

17.
$$H_2O_2 + 2KI \xrightarrow{40\% \text{ yield}} I_2 + 2KOH$$

 $H_2O_2 + 2KMnO_4 + 3H_2SO_4 \xrightarrow{50\% \text{ yield}}$

 $K_2SO_4 + 2MnSO_4 + 3O_2 + 4H_2O$ 150 mL of H₂O₂ sample was divided into two parts. First part was treated with KI and KOH formed required 200 mL of M/2 H₂SO₄ for neutralisation. Other part was treated with KMnO₄ yielding 6.74 L of O_2 at STP. The molarity of H_2O_2 is

- 18. In a reaction at equilibrium, 'x' moles of the reactant A decompose to give 1 mole each of C and D. If the fraction of A decomposed at equilibrium is independent of initial concentration of A, then the value of *x* is
- 19. How many compounds (including stereoisomers) with molecular formula, C₅H₁₀O may be reduced with NaBH₄ to a primary alcohol.

- 20. 1.6 g of pyrolusite was treated with 50 cm³ of 1.0 N oxalic acid and some H₂SO₄. The oxalic acid left undecomposed was raised to 250 cm³ in a flask. 25 cm³ of this solution when treated with 0.1 N KMnO₄ required 32 cm³ of the solution. Calculate the % of available oxygen? (At. mass of Mn = 54.9)
- 21. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO3 and the volume made to 100 mL. A silver electrode was dipped in the solution and EMF of the cell set up was 0.62 V.

Pt_(s), H_{2(g)} | H⁺ (1 M) ||Ag⁺_(aq)|Ag_(s)
The % of Ag in the alloy is
$$[E^{\circ}_{cell} = 0.80 \text{ V}, 2.303RT/F = 0.06 \text{ at } 25^{\circ}\text{C},$$
 At. mass of Ag = 108 u]

22.
$$H_2C = O + D_2C = O \xrightarrow{conc. NaOH} Cannizzaro's$$
 products

Find the number of alcohols that would be formed by the above reaction?

ANSWERS

1.	(a)	2.	(a)	3.	(a)	4.	(d)	5. (d)
6.	(a)	7.	(b)	8.	(a, b	, c, d)	9. (a, c, d)
10.	(a, d	11.	(b, d	l)		12.	(c)	13. (d)
14.	(c)	15.	(a)	16.	(c)	17.	(3)	18. (2)
19.	(5)	20.	(9)	21.	(1)	22.	(4)	

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EMISTRY MUSING

- 1. (a) : Eq. of metal = $\frac{0.43}{E}$ (E is eq. wt. of metal) $\therefore \text{ Meq. of metal} = \frac{0.43}{E} \times 1000 = \frac{430}{E}$
- Meq. of total H_2SO_4 solution = $1 \times 50 = 50$ Meq. of H_2SO_4 reacted with metal = Meq. of the metal

 \therefore Meq. of unreacted H₂SO₄ = $\left(50 - \frac{430}{E}\right)$

Meq. of unreacted H₂SO₄ = Meq. of NaOH = 1×14.2 $\therefore 50 - \frac{430}{E} = 1 \times 14.2 \implies E = 12.01$

- **2. (b)**: The graph of $\Delta_f G^{\circ}$ vs T in the Ellingham diagram shows that Cu-Cu₂O line is almost at the top (i.e., much higher than those of Al-Al₂O₃, Mg-MgO, Zn-ZnO and Fe-FeO lines). Therefore, Cu₂O can be reduced to Cu at the lowest temperature by carbon.
- 3. (d): Ionic conductance of ion = Transport no. of that ion $\times \Lambda_{ea}^{\circ}$ of strong electrolyte containing that ion $= (1 - 0.40) \times 160.84 = 96.504$

 $\frac{\text{Ionic conductance}}{96,500} = \frac{96.504}{96,500} = 10^{-3}$

4. (b):

4. (b):
$$CH_{3} \longrightarrow NO_{2} \xrightarrow{Br_{2}} CH_{3} \longrightarrow NO_{2}$$

$$NO_{2} \xrightarrow{bromination} CH_{3} \longrightarrow NO_{2}$$

$$\frac{\text{Sn/HCl}}{\text{(Reduction)}} \text{CH}_{3} \longrightarrow \text{NH}_{2} \frac{\text{NaNO}_{2}/\text{HCl}}{273-278 \text{ K}}$$

$$CH_{3} - \bigvee_{(C)}^{+} - \bigvee_{N=1}^{+} NCl^{-} \xrightarrow{H_{3}PO_{2}/H_{2}O \\ -N_{2}, -HCl}$$
(Reduction)

$$CH_{3} \xrightarrow{Br} \xrightarrow{KMnO_{4},OH^{-}} HOOC \xrightarrow{Br}$$

$$(D) \xrightarrow{(Oxidation)} HOOC \xrightarrow{(E)}$$

5. (a): Mineral spinel, MgAl₂O₄ in which oxide ions are arranged in *ccp* or *fcc* with dipositive Mg²⁺ ions in the tetrahedral voids and tripositive Al³⁺ ions in octahedral voids. No. of oxide ions = 4

No. of octahedral voids = 4

No. of tetrahedral voids = 8

No. of Mg^{2+} ions in tetrahedral voids = 1 No. of Al^{3+} ions in octahedral voids = 2

Thus, $\frac{1}{8}$ th of the tetrahedral voids and $\frac{1}{2}$ th of the octahedral voids are occupied.

6. (c): As $t_{1/2} = 1590$ years, therefore, in 1590 years, half of the amount of Ra will disintegrate,

i.e., amount of Ra disintegrated = $0.5 \text{ g} = \frac{0.5}{226} \text{mole}$

As each Ra nucleus produces four α-particles, therefore,

helium produced = $\frac{0.5}{226} \times 4$ mole = 8.85×10^{-3} mole

$$PV = n RT \implies P = \frac{nRT}{V}$$

$$= \frac{(8.85 \times 10^{-3} \text{ mole})(0.0821 \text{L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}{5 \times 10^{-3} \text{L}}$$

= 43.59 atm

7. (d): Reaction for the combustion of methanol is $2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$

$$\Delta_r G^{\circ} = \left[2\Delta G_{\text{CO}_2}^{\circ} + 4\Delta G_{\text{H}_2\text{O}}^{\circ} \right] - \left[2\Delta G_{\text{CH}_3\text{OH}}^{\circ} + 3\Delta G_{\text{O}_2}^{\circ} \right]$$
$$= \left[2 \times (-394.4) + 4 \times (-237.1) \right] - \left[2 \times (-166.3) + 3 \times 0 \right]$$

= -1737.2 + 332.6 = -1404.6

$$\Delta_f G_{\text{CH}_3\text{OH}}^{\circ} = \frac{-1404.6}{2} = -702.3 \text{ kJ mol}^{-1}$$

8. **(b)**:
$$\Delta n_g = 1 - \frac{3}{2} = \frac{2-3}{2} = \frac{-1}{2} = -0.5$$

$$-726 = \Delta E - (0.5) \times 8.314 \times 298 \times 10^{-3}$$

 $\Delta E = -726 + 1.24 = -724.76 \text{ kJ mol}^{-1}$

$$\Delta E = -726 + 1.24 = -724.76 \text{ kJ mol}^{-1}$$

9. (6):
$$N_2O_{5(g)} \longrightarrow N_2O_{4(g)} + \frac{1}{2}O_{2(g)}$$

Initial pressure 114 mm 0 0

After 25 min.
$$114 - p \qquad P$$
Total pressure = $(114 - p) + p + \frac{1}{2}p$

 $=114 + \frac{1}{2}p = 133 \,\text{mm}$ (Given)

$$\therefore \quad \frac{1}{2}p = 19 \quad \text{or} \quad p = 38 \text{ mm}$$

To convert it into mol L⁻¹, apply pV = n RT, *i.e.*,

$$\frac{n}{V} = \frac{p}{RT}$$

∴ Decrease in molar concentration of N₂O₅

$$= \frac{38/760 \text{ atm}}{0.0821 \text{ L atm K}^{-1} \text{mol}^{-1} \times 400 \text{ K}} = 0.0015 \text{ mol L}^{-1}$$

$$\frac{-0.0821 \,\text{L atm K}^{-1} \text{mol}^{-1} \times 400 \,\text{K}}{0.0821 \,\text{L atm K}^{-1} \text{mol}^{-1} \times 400 \,\text{K}}$$
∴ Average rate of reaction =
$$\frac{0.0015 \,\text{mol L}^{-1}}{25 \times 60 \,\text{s}} = 10^{-6} \text{mol L}^{-1} \text{s}^{-1}$$

10. (4):
$$\frac{x}{m} = k P^{1/n}$$
 or $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$

 \therefore Plot of $\log \frac{x}{m}$ versus $\log P$ is linear with

slope =
$$\frac{1}{n}$$
 and intercept = $\log k$.

Thus,
$$\frac{1}{n} = \tan \theta = \tan 45^{\circ} = 1$$
 or $n = 1$

$$\log k = 0.3010 \text{ or } k = 2$$

log
$$k = 0.3010$$
 or $k = 2$
At $P = 2$ atm, $\frac{x}{m} = k P^{1/n} = 2 \times (2)^1 = 4 g$

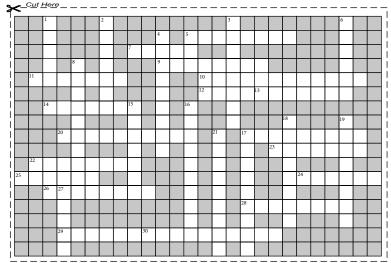


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ACROSS

- 5. A thermodynamic quantity that measures the effective concentration of a particular substance in a given chemical system. (8)
- 7. The characteristic organic constituent of the soil. (5)
- **9.** CCl₄ hydrolyses with superheated steam in presence of iron to form _____. (8)
- **10.** Neutral particle produced in nuclear beta decay. (12)
- **11.** Compound in which two same functional groups are bonded to the same carbon atom. (7)
- **12.** A bond which is parallel to the axis of the ring in cyclohexane. (5)
- **13.** The regular three-dimensional array of atoms in a crystral. (7)
- **14.** Substance that arrest a change in the pH value when it is added to an acidic or basic solution. (6)
- 17. A group of organosilicon polymers. (9)
- **20.** Different solutions having same vapour pressure are called ______ solutions. (10)
- **22.** Solid particles or liquid droplets enclosed under pressure and released as a fine spray by means of propellant gas (7).
- **23.** Stereoisomers that differ in configuration at the hemiacetal carbon. (7)
- 24. A gas which has inversion temperature, 33 K. (6)
- 25. Mixed chlorofluorocarbons. (6)
- **26.** Carbohydrates are stored in animal body as _____. (8)
- **28.** The process by which air is mixed with or dissolved in liquid or substance. (8)
- **29.** Many neurotransmitters are ______including epinephrine, serotonin, norepinephrine, etc. (6)
- **30.** The lowest temperature at which the application of a small flame causes the vapour above a flammable liquid to ignite when the liquid is heated under standard condition. (10)



DOWN

- 1. Concentrated solution of NaCl in water. (5)
- **2.** IUPAC name of ethylene oxide. (7)
- **3.** The study of the rate of reaction. (8)
- **4.** A synonym of amphoteric electrolyte. (9)
- **6.** An organic compound containing >C=C=O functional group. (6)
- **8.** The net movement of molecules or atoms from a region of high concentration to a region of low concentration. (9)
- **15.** A metal complex with one or more polydentate ligand is . (7)
- **16.** Pharmaceutical solutions made by boiling of dissolved chemicals from herbal or plant materials. (10)
- 17. A strong acid that exists as a solid at room temperature. (9)
- 18. The principal ore of mercury. (8)
- 19. Particles with half integral spin. (8)
- **21.** The determination of molecular weight by the freezing point depression method. (9)
- 27. Spectral series found in atomic hydrogen that lies in UV region. (5)

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